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NICKEL-CHROMIUM ALLOYS ADAPTED FOR USE IN CONTACT WITH MOLTEN GLASS

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ABSTRACT OF THE DISCLOSURE

Nickel-base alloys containing correlated percentages of carbon, chromium, tungsten, tantalum and preferably zirconium afford good corrosion resistance and exhibit highly satisfactory elevated temperature properties (circa 1080° C.), characteristics which render the alloys particularly suitable for use in contact with such media as molten glass.

As is generally known by those skilled in the art, a considerable number of diverse metals and alloys have been proposed and used for high temperature applications, applications which also often demand exceptional resistance to various corrosive media. Illustrative of this are the many situations in which the handling of molten glass is encountered. In historical perspective it has been the precious metals and alloys thereof which have found extensive use, generally speaking, in molten glass environments but, as would be expected, the relatively high cost of such materials has always been an inherent drawback.

In the continuous search for less expensive materials, a variety of alloys has been investigated, and the nickel-base materials have received particular attention in view of their generally good corrosion behavior and ability to resist the effects of high temperature. One such alloy, used as spinners in the production of glass fibers, contains about 52% nickel, 25% chromium, 5% tungsten, 0.5% carbon, the balance being iron. However, while this alloy has given good service, spinners fabricated therefrom cannot be gainfully used at temperatures exceeding about 1030° C. (even at 1030° C. their life under actual operating conditions is relatively short). This aspect serves to emphasize that more than good corrosion resistance and lower cost is necessary. For if the more stringent conditions brought about by higher operating temperatures are to be successfully met, a new combination of elevated temperature characteristics is required. Accordingly, there is need for an alloy having improved properties such that it can be used at temperatures well above 1030° C. e.g. 1080° C. or above (or which has a longer useful life at lower operating temperatures).

It has now been discovered that certain nickel-base alloys containing special amounts of carbon, chromium, tungsten, tantalum and zirconium, provide an improved combination of stress rupture characteristics and resistance to creep at temperatures above 1030° C., e.g., 1080° C. or higher, while concomitantly manifesting a high degree of resistance to the corrosive and erosive action of molten glass.

It is an object of the present invention to provide novel and useful nickel-base alloys possessing satisfactory elevated temperature properties.

Another object of the present invention is to provide nickel-base alloys which greatly resist the corrosive and erosive effects of molten glass.

A further object of the present invention is to provide articles of manufacture fabricated from alloys of the invention for use in contact with molten glass.

Other objects and advantages will become apparent from the following description.

In accordance with the invention, an optimum combination of properties can be achieved with the preferred alloy contemplated herein containing (by weight) from about 0.3% to 1% carbon, from about 25% to 35% chromium, from about 3% to about 8% tungsten, from about 2% to 8% tantalum, a small but effective amount, e.g. about 0.1% and up to about 0.5% zirconium, up to 0.05%, e.g. 0.005% to 0.5% boron, the balance being essentially nickel, the nickel preferably being at least 56%. As will be understood by those skilled in the art, the use of the expression "balance" or "balance essentially" in referring to the nickel content of the alloys does not exclude the presence of other elements commonly present as incidental constituents, e.g. deoxidizing, malleabilizing and/or cleansing elements, and impurities normally associated therewith in small amounts which do not adversely affect the basic characteristic of the alloys. However, in respect of the constituents iron, silicon and manganese, the amounts of these elements should not exceed 2%, 0.5% and 0.5% respectively; otherwise, the stress rupture and creep properties would be adversely affected. Broadly speaking, when the best properties are not required zirconium may be absent from the alloys as explained hereinafter, and such zirconium-free alloys are in accordance with the invention.

In carrying the invention into practice, if the carbon content of the alloy should fall much below about 0.3% stress-rupture life is considerably impaired and the ability to resist excessive creep is adversely affected. On the other hand, if the carbon content exceeds 1% poorer properties are obtained and in particular the ductility and impact resistance are reduced to unacceptable values. It is quite advantageous that the carbon content be from about 0.4% to 0.6%.

With regard to chromium, percentage above 35% adversely affect creep strength and while the chromium content may be as low as 25%, in achieving the best combination of properties, it is most beneficial that the chromium level be not less than about 28%. Where alloys are required which consistently manifest the best combination of creep strength and corrosion resistance, a chromium range of 28% to 32% is highly satisfactory.

Considerable care must also be exercised in respect of tungsten. While in many nickel-base and other alloys broad ranges of tungsten can be utilized, that is not the case with the subject alloys. It has been found, for example, that even amounts of but 10% (versus the upper limit of about 8%) greatly detract from stress rupture strength and creep resistance. However, tungsten is necessary for hardening the alloys by solid-solution hardening and by carbide formation and at least about 3% tungsten must be present for this purpose. It is most preferred that the tungsten content not exceed about 6%, and a range of 4% to 6% gives excellent results. With regard to tantalum, high temperature properties are, in the absence thereof, seriously impaired and in this connection from 4% to 5% or 6% tantalum is quite beneficial.

Zirconium confers a most pronounced effect in respect of stress-rupture life. Amounts as low as about 0.28% have been found to more than double the stress rupture life of the alloys at the extremely high temperature of 1150° C. (approximately 2102° F.). Furthermore, and simultaneously therewith (in comparison with a comparable but zirconium-free alloy), this same small amount of zirconium has been found to impart remarkable creep resistant qualities as will be illustrated herein. However, it appears that as the zirconium content is increased a maximum is reached in its effectiveness in improving creep strength. The zirconium content at which the maximum improvement is achieved probably depends on the temperature at which the alloy is tested or used. Also the choice of zirconium content may be governed by the need for an optimum combination of stress-rupture strength and creep resistance. In achieving highly satisfactory results a zirconium range of about 0.15% to 0.3% or 0.35% is extremely beneficial.

Boron detracts from stress rupture life, as shown by stress rupture tests at 1150° C., and when the best possible stress rupture life is required boron should be absent, The presence of boron does, however, enhance the creep resistance of the alloys. For this reason it is possible to achieve a useful combination of stress rupture strength and creep resistance by suitably balanced additions of both boron and zirconium. Satisfactory results may be obtained, for example, by incorporating in the alloys from about 0.1% to about 0.5% zirconium and from about 0.005% to about 0.05% boron, e.g. from 0.15% to 0.25% zirconium and from 0.01% to 0.03% boron.

A comparison of Alloys A and 1 clearly reflects the subversive influence attributable to tungsten when appreciably present to the excess. Both stress rupture life and resistance to creep were greatly adversely affected, the latter by a factor of ten. This damaging effect is even more pronounced when the alloy is also low in carbon as can be seen by reference to Alloy B (0.15% carbon vs. 0.5% carbon for Alloy 1.) The degradation caused by low carbon is further confirmed by a comparison of Alloys 2 and C, and 1 and D. Alloys 1 and 2 also indicate that highly satisfactory results flow from tantalum contents over the range of 3% to 6%.

To illustrate the beneficial effects attributable to the presence of zirconium per se, various data are given in Table II, the alloys being prepared and tested in the same manner as those set forth in Table I. (Alloys 3 through 8 are within the invention.)

Also included are data concerning the effect of boron.

TABLE II

	Composition [1]						Stress-rupture properties at 1 t.s.i./1,150° C.		Creep strain at 1.27 t.s.i. 1,080° C.	
Alloy	C (percent)	Cr (percent)	W (percent)	Ta (percent)	Zr (percent)	B (percent)	Life (hours)	Elongation (percent)	Time (hours)	Strain (percent)
3	0.47	29.5	4.9	4.5	[2] N.A.	N.A.	178	13.2	312	2.44
4	0.49	29.8	5.2	4.6	0.20	N.A.	259	14.1	312	0.54
5	0.48	29.5	5.0	4.5	0.33	N.A.	460	12.6	312	0.62
6	0.49	29.8	5.0	4.3	0.16	0.020	-----	-----	310	0.39
7	0.58	29.8	4.9	4.3	0.24	0.020	262	9.6	-----	-----
8	0.51	29.4	5.0	4.6	0.29	0.015	255	11.3	309	0.49

[1] Balance nickel and impurities.
[2] N.A. indicates that the element was not added.

Alloys in accordance with the invention and containing neither zirconium nor boron have a fairly satisfactory stress rupture life but do not have the excellent creep resistant characteristic of the alloys containing zirconium or boron However, the creep properties of these alloys are adequate for many purposes.

Where resistance to creep is of paramount importance and stress rupture life can be sacrificed boron, e.g. up to 0.01% or 0.03%, can be present in the absence of zirconium.

For the purpose of giving those skilled in the art a better understanding of the invention, the following illustrative data are given. A series of alloys were vacuum melted in an electric induction furnace. Nickel, chromium, tungsten and carbon were first charged into the furnace and the pressure reduced to 1 micron (of mercury). The pump was isolated and the charge melted. After reducing the pressure again, to 5 microns, and holding for 10 minutes, tantalum was added. After holding for 15 minutes at 1 micron and 1520° C., zirconium (as nickel-zirconium) or boron (as nickel-boron) or both were added when required in the alloy. The alloys were then cast at 1550° C. into hot refractory molds. Specimens were machined from the alloys and then tested in the as-cast condition and the results are reported in Table I. In this regard and apart from the given amounts (nominal) of carbon, tungsten and tantalum each of the alloys contained nominally 30% chromium, 0.2% zirconium and 0.02% boron, the balance being nickel and impurities. Alloys 1 and 2 are within the invention. Alloys A through D being outside the scope thereof. Also set forth in Table I are the conditions of test.

The data given in Table II indicate the excellent properties which may be obtained in alloys in accordance with the invention. In this respect particular attention is drawn to Alloys 4 through 8, which contain zirconium. A comparison of Alloys 3 and 5, for example, clearly demonstrates the potent influence attributable to the presence of zirconium, rupture life being increased by over 150% with resistance to creep also being markedly improved. While resistance to creep was further enhanced by the presence of boron, a reduction in stress-rupture life at 1150° C. was experienced.

As discussed herein, where shorter stress rupture lives can be tolerated, the alloys may contain boron in the absence of zirconium. A further alloy, Alloy 9, is an example of such an alloy. Alloy 9 contained 0.49% carbon, 29.8% chromium, 4.9% tungsten, 4.6% tantalum and 0.015% boron, the balance being essentially nickel. Alloy 9 was prepared and tested in the same manner as the alloys set forth in Table I. After 310 hours at 1080° C. under a stress of 1.27 t.s.i. Alloy 9 showed a creep strain of 0.69%.

As indicated above herein, the alloys contemplated herein can be prepared using vacuum techniques. In this connection conventional melting and casting techniques can be used in producing the alloys. To ensure retention of a desired amount of any zirconium or boron these elements should be added to the melt immediately prior to casting. Satisfactorily nickel, chromium, tungsten and carbon are first charged to the furnace and after melting and holding at less than 100 microns pressure and preferably less than 5 microns pressure for up to 15 minutes, e.g. 10 minutes, tantalum is added. The melt

TABLE I

				Stress rupture properties				Creep strain at 1.27 t.s.i.[1]/1,080° C.	
				2.7 t.s.i.[1]/1,000° C.		1 t.s.i.[1]/1,150° C.			
Alloy	C (percent)	W (percent)	Ta (percent)	Life (hours)	Elongation (percent)	Life (hours)	Elongation (percent)	Time (hours)	Strain (percent)
A	0.5	10	3	249	24	120	10.8	312	6.4
1	0.5	5	3	472	26	172	15.0	310	0.58
B	0.15	10	3	126	41	-----	-----	197	11.7
2	0.5	5	6	518	14.7	158	-----	310	0.61
C	0.15	5	6	105	35	108	10	312	6.7
D	0.15	5	3	-----	-----	[2]71	-----	-----	-----

[1] Long tons per square inch.
[2] Average of two values.

is then held at less than 10 microns pressure and preferably less than 1 micron pressure for 10 to 30 or 60 minutes, e.g. 15 minutes, both holding treatments being carried out between 1400 and 1600° C. but preferably between 1500 and 1550° C., e.g. 1520° C. The duration of the second holding treatment depends on the purity of the ingredients of the melt, longer time being required when less pure ingredients are employed. Zirconium or boron may then be added, e.g. as nickel-zirconium or nickel-boron. The alloy is then cast at 1500° C. to 1600° C., e.g. at 1530 to 1570° C.

Air melting practice may be used if desired but great care should be taken that there is sufficient zirconium or boron retained when these elements are required and for this purpose the melt should be deoxidised immediately prior to the addition of zirconium or boron.

While the alloys in accordance herewith are useful in applications involving molten glass (including flowing molten glass), e.g. centrifugal spinners for the manufacture of glass fibre, they can be employed in many other areas of application where resistance to corrosion at elevated temperatures in combination with good creep and stress rupture resistance is required, e.g. in industrial chemical plant.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and appended claims.

I claim:

1. A nickel-base alloy consisting essentially of about 0.3% to about 1% carbon, from 25% to 35% chromium, about 3% to about 8% tungsten, about 2% to about 8% tantalum, up to about 0.5% zirconium, up to about 0.05% boron and the balance essentially nickel.

2. An alloy in accordance with claim **1** which contains at least 28% chromium.

3 An alloy in accordance with claim **1** in which the tungsten content does not exceed 6%.

4. An alloy in accordance with claim **1** containing about 0.4% to about 0.6% carbon, about 28% to about 32% chromium, about 4% to about 6% tungsten and about 4% to 6% tantalum.

5. As a new article of manufacture, a component fabricated from the alloy set forth in claim **1** for use in contact with molten glass.

6. As a new article of manufacture, a component fabricated from the alloy set forth in claim **4** foı use in contact with molten glass.

7. A nickel-base alloy consisting essentially of about 0.3% to about 1% carbon, from 25% to 35% chromium, about 3% to about 8% tungsten, about 2% to about 8% tantalum, zirconium in a small but effective amount sufficient to enhance the stress-rupture life of the alloy the amount of zirconium being up to about 0.5%, up to about 0.05% boron and the balance essentially nickel.

8. An alloy in accordance with claim **7** which contains at least 28% chromium.

9. An alloy in accordance with claim **7** which contains at least 0.1% zirconium.

10. An alloy in accordance with claim **7** in which the tungsten content does not exceed 6%.

11. An alloy in accordance with claim **7** containing about 0.15% to 0.35% zirconium.

12. An alloy in accordance with claim **7** containing about 0.4% to about 0.6% carbon, about 28% to about 32% chromium, about 4% to about 6% tungsten, about 4% to about 6% tantalum and about 0.15% to 0.35% zirconium.

13. An alloy in accordance with claim **7** containing from 0.1% to 0.5% zirconium and from 0.005% to 0.05% boron.

14. An alloy in accordance with claim **12** containing from 0.15% to 0.25% zirconium and from 0.01% to 0.03% boron.

15. An alloy in accordance with claim **7** characterized by good stress rupture life and the ability to resist creep at temperatures on the order of about 1080° C.

16. As a new article of manufacture, a component fabricated from the alloy set forth in claim **7** for use in contact with molten glass.

17. As a new article of manufacture, a component fabricated from the alloy set forth in claim **12** for use in contact with molten glass.

References Cited

UNITED STATES PATENTS

3,316,074	4/1967	Laurent et al. --------	75—171
3,318,694	5/1967	Heitmann -----------	75—171

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U.S. Cl. X.R.

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