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CAST VALVE

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The present invention relates to cast valves and other castings of nickel-copper alloys which in use are subjected to elevated temperatures, and, in some cases, to pressure or other stresses.

For certain applications, valves and other castings are required which are capable of operating at elevated temperatures of the order of several hundred degrees Fahrenheit. In many cases the castings not only are required to withstand pressure and/or other stresses, but also must be resistant to corrosive agents that come in contact therewith. For example, steam pressure valves used in railroad locomotives may operate at temperatures of about 750° F. and 400 lbs. per square inch pressure.

Certain alloys comprised predominantly of nickel and copper, the nickel always being in excess of the copper, have desirable casting and corrosion resisting properties for the production of valves and other castings of this general type but the strength properties decrease so appreciably in the neighborhood of 800° F. that some manufacturers have not specified these alloys for use in valves and castings which must operate at temperatures of 750° F. and above.

We have discovered that the strength of nickel-copper castings at elevated temperatures as indicated by both long and short time tensile tests can be greatly improved by the addition of zirconium in controlled and critical amounts. The elongation of the zirconium-containing nickel-copper alloys at elevated temperatures shows a startling increase over that of zirconium-free alloys of comparable composition, and this is extremely important to provide safety and resistance to overloads as well as to give proper warning prior to fracture if the casting is grossly overloaded in use.

It is an object of the present invention to provide castings of nickel-copper alloy having improved strength properties, particularly improved elongation and resistance to continuously applied stresses at elevated temperatures.

It is a further object of the present invention to provide cast valves of nickel-copper alloys which may be subjected in use to temperatures above 700° F. up to about 1000° F., and in specific instances as high as about 1100° F.

Other objects and advantages of the present invention will become apparent from the following detailed description of the invention.

Generally speaking, the present invention is based on the discovery made by us that the addition of zirconium in controlled and critical amounts to nickel-copper casting alloys greatly improves the short time and long time tensile strength and elongation at elevated temperatures, particularly at temperatures of about 800° F. and higher.

In short time high temperature tensile tests nickel-copper alloys containing no zirconium possess high strength and high ductility at temperatures up to about 700° F. and exhibit a transcrystalline fracture. At about 800° F. a small part of the fracture becomes intercrystalline or dendritic. Above about 800° F. the fracture becomes more and more dendritic until at about 900° F. it is completely so. This change in the nature of the fracture is accompanied by a sharp and considerable drop in strength and particularly elongation. The presence of zirconium as an alloying element in the nickel-copper casting from effective amounts up to about 1% overcomes the tendency of the metal to fracture intercrystallinely in the temperature range of about 800 to over 1000° F.

For example, the presence of about 0.35% zirconium as an alloying element in a cast nickel-copper alloy yields high strength and high elongation at temperatures in excess of 1000° F. The tensile strength and elongation of this alloy at about 1000° F. corresponded roughly with the properties of a comparable zirconium-free alloy at 800° F., an improvement of over 200° F. The improvement of the short time high temperature tensile properties of regular cast nickel-copper

alloy by the addition of various amounts of zirconium may be seen from Table I.

The increase in tensile strength and elongation at elevated temperatures produced by the

Table I

Specimen No.	C	Zr	Tensile strength*				Nature of fracture			Elongation	
			800° F.	900° F.	980° F.	1100° F.	800° F.	900° F.	980° F.	900° F.	980° F.
	Percent	Percent								Percent	Percent
1.....	.17	0	53.9	39.8	30.7	-----	T (I)	T-1	I	17.5	3.0
2.....	.15	0	49.3	32.6	-----	-----	T (I)	T-1	-----	24	-----
3.....	.15	.06	-----	51.1	46.4	-----	-----	-----	-----	45	40
4.....	.18	.12	-----	56.5	48.5	-----	-----	-----	-----	41	30
5.....	.17	.35	-----	57.4	52.0	40.2	-----	T	T	33	30
6.....	.18	.59	-----	52.7	49.7	-----	-----	-----	-----	25.5	25
7.....	.11	.76	-----	38.9	43.3	-----	-----	-----	-----	13	22.5

Base composition about 28.21% Cu, 0.75% Mn, 1.59% Fe, 1.3% Si, balance Ni.

*Thousand pounds per sq. in.

T—Transcrystalline.

T(I)—Mainly transcrystalline, small amount of intercrystalline.

T-1—Roughly half transcrystalline, half intercrystalline.

I—Inter-crystalline at 1100° F. Specimen No. 5 exhibited intercrystalline fracture.

From data in the foregoing table it will be apparent that the tensile strength of the nickel-copper alloy is greatly improved at 900° F. by about 0.05% to about 0.60% zirconium, the maximum tensile strength being obtained at this temperature with a zirconium content of about 0.10% to 0.40%. The tensile strength at 900° F. falls on further increase in zirconium content but even at 0.76% zirconium the strength is higher than a comparable zirconium-free alloy. The 0.06% zirconium alloys showed the maximum elongation at this temperature. The elongation decreased with higher content of zirconium but the 0.76% zirconium alloy still possessed an elongation approximately that of zirconium-free alloys.

At 980° F. the maximum tensile strength occurs in the alloys containing about 0.35% zirconium and even at about 0.75% zirconium the strength is substantially greater than with zirconium free alloys. Over the whole range of about 0.05% to about 0.75% zirconium at 980° F. the elongation is from about 700% to 1000% higher than in zirconium-free alloys.

In long time step loading high temperature "time to fracture" tests conducted at 800° F. specimens were initially stressed in tension at about 35,000 lbs. per square inch and held until fracture occurred or until approximately a week had elapsed. Those specimens which had not fractured were then stressed at a load 5000 lbs. per square inch higher for approximately a week, after which the stress was raised another 5000 lbs. per square inch, etc., until the test was terminated by fracture. The following results were obtained:

Table II

Specimen No.	Zr	Time in hours under various stresses					Total time to fracture	Elongation at fracture
		*35,000	*40,000	*45,000	*50,000	*55,000		
	Percent						Hours	Percent
8.....	0	**130	-----	-----	-----	-----	130	8
9.....	.07	165	170	**165	-----	-----	500	29
10.....	.35	160	170	165	**20	-----	515	21
11.....	.59	165	170	165	**2	-----	502	18
12.....	.76	165	170	170	240	(***)	745	22

* Pounds per square inch.

** Failure occurred.

*** Failure occurred as stress was being raised to 55,000 p. s. i.

These data clearly show the marked improvement of the zirconium-containing nickel-copper castings over zirconium-free alloys for use under more or less continuous stress at elevated temperatures.

addition of zirconium to the nickel-copper casting alloys is surprising inasmuch as the room temperature tests show that the tensile strength and elongation decrease progressively as zirconium is added. Data illustrating the decrease in room temperature tensile strength and elongation are assembled in Table III.

Table III

Specimen No.	Zr content	Tensile strength*	Elongation
		Percent	Percent
13.....	0	82,000	38
14.....	.12	76,750	35
15.....	.22	79,750	36
16.....	.59	68,200	25
17.....	.76	54,200	24

* Pounds per sq. in.

The preferred zirconium content will depend somewhat upon the temperature at which the casting is designed to operate and the relative weight attached to short time and long time tensile or creep properties. At operating temperatures up to about 900° F. the preferred zirconium content will approximate about 0.04 to 0.50%. When the operating temperature approaches 1000° F., the optimum range may go as high as 0.60% zirconium. On the basis of time to fracture tests at 800° F., giving some indication of creep strength, a zirconium content of about 0.75% appears to be advantageous. At somewhat lower temperatures zirconium from an effective amount of about 0.02% or 0.03% up to about 0.20% gives an advantageous combination of properties. Balancing room temperature

properties with high temperature properties, castability, cost and reliability of production, the zirconium content for general high temperature applications preferably will lie within the range of about 0.05 to 0.30%.

The zirconium may be added to the molten casting alloy in any suitable form. Satisfactory results have been obtained using commercial silicon-zirconium alloy containing about 48% silicon, 41% zirconium, and the balance principally iron. Similarly, a special zirconium-nickel alloy (70% zirconium, 30% nickel) of high purity has given satisfactory results. The melt should be preliminarily deoxidized with a suitable deoxidizer, e. g., silicon, manganese, and the like, prior to adding the zirconium. In making nickel-copper alloys it is generally necessary to add an element having high affinity for sulfur, e. g., magnesium, calcium and the like, as a desulfurizing or sulfur fixing agent. We generally prefer to use magnesium, ordinarily within a range of about 0.05 to 0.10%, added to the ladle just before pouring. Within the amounts contemplated by the present invention, particularly within the preferred range, zirconium does not deleteriously affect the casting properties provided silicon, manganese and carbon are present in proper amounts. Ordinarily the valve body and other castings of the present invention will be poured into sand molds, although for certain castings of relatively simple geometric form, centrifugal and other casting methods may be used. The recovery of zirconium has been found to vary under ordinary conditions from about 50 to 75%.

The silicon content may vary from about 0.5 to 5%, the maximum amount present in the alloy depending upon the nickel content and hardness desired. For general purposes silicon should fall within the range of about 1 to 1.5%. When silicon exceeds about 3% in an alloy containing about 65% nickel, the alloy shows marked increase in hardness and decrease in ductility, but due to its high resistance to galling and steam erosion, it is valuable for certain special purposes such as valve elements and similar high temperature applications which are exposed to sliding friction, particularly for valve seats. In alloys of this type, the silicon content apparently exceeds the limit of solid solubility and is present in or forms part of a precipitated phase. The amount of silicon required to produce equivalent microstructure increases with the nickel content. For instance, 2.5% silicon at 50% nickel yields substantially the same type of microstructure as 4.25% silicon at 67% nickel. An alloy containing about 2.5% silicon with about 65% nickel finds use where lower hardness but higher ductility than obtained with 4% silicon is required. A silicon content of about 1 to 1.5%, typically about 1.25%, should be used in castings for general high temperature applications where machinability, ductility, strength and castability are important considerations.

The presence of another easily oxidizable element such as iron and/or manganese is essential for high fluidity and good castability and generally both are present in small amounts. We prefer to have from .5 to 1.5% manganese present although higher percentages of the order of 2% or even 3% are sometimes used for special purposes. We have observed that 5% manganese seems to reduce the ductility of the zirconium-containing alloys at about 980° F. although the strength remained high. Except in the high silicon castings, referred to above, the iron content should be maintained approximately within the limits of solid solubility at the working temperature. The maximum amount of iron soluble in the alloy will increase somewhat with

the nickel content. Ordinarily the amount of iron should not exceed about 5%. In an alloy containing about 67% nickel the presence of about 5% iron mildly increased the tensile strength at 800° F. but appreciably decreased the elongation as compared with an alloy of the same base composition containing about 1.5% iron. Alloys free from iron can be made, where desired, if manganese be present. Where iron is in amounts of the order of 1% is present, the manganese is less essential and good castings can be made with little or none of that element present. Generally the iron content will be under 2.5%, 1.5 to 2.0% being usual.

The carbon content ordinarily is maintained between about 0.04% and 0.35%, preferably within the range of about 0.10% to 0.25%. Carbon up to about 0.6% may be present in some castings. Generally speaking, at low zirconium levels in alloys containing about 69% nickel, 1.25% silicon and the balance largely copper, the tensile strength increases with the carbon content up to about 0.30%. The ductility decreases somewhat at higher carbon levels due to the formation of graphite. The tendency of the carbon in the alloys to graphitize is accentuated by increasing the silicon content, and less sharply by increasing the copper content. The presence of larger amounts of zirconium appears to suppress somewhat the tendency of the carbon to graphitize. Data illustrating the effect of different carbon contents on the high temperature tensile strength and elongation of an alloy having substantially the same base composition as the specimens of Table I are given in Table IV.

Table IV

Specimen No.	C	Zr	Tensile strength*	Elongation*
	Percent	Percent		Percent
18.....	.04	.23	51,600	35
19.....	.10	.33	55,250	37
20.....	.29	.33	60,400	28

* At 900° F.

It will be seen from the data in Table IV that within the carbon range of about 0.04% to about 0.30% the tensile strength increases with the carbon content. It is particularly important to note that the elongation remained high in all cases.

The copper and nickel content may vary rather widely. Ordinarily the nickel content will be maintained between about 50% and 90%, preferably within the range of about 60% to 70%. Nickel ordinarily contains a small amount of cobalt and in the specification and claims the term "nickel" is used to designate the combined nickel and cobalt content. The maximum amount of cobalt which may be present is approximately the same as iron, described hereinabove. The copper content must exceed about 10% and will constitute the balance of the alloy. Copper may be as high as about 48%, although preferably lying within the range of about 25 to 35%. When the term "balance copper" or "balance nickel" is used in the description or the claims, it is to be construed as including within its scope any impurities that may be present, e. g., those traceable to the ores or manufacturing process used in preparing the alloys, as well as any other elements normally present in nickel-copper casting alloys for high temperature applications which may also be present in the castings of the present invention without departing from the scope

thereof, e. g., deoxidizers and carbide formers such as titanium in small amounts.

The presence of zirconium appears to have a beneficial action in tending to eliminate thermal cracks in the nickel-copper alloy castings. Thus in the castings made of the high silicon alloy mentioned above where it is necessary to quench or rapidly cool the casting to soften it, the tendency to crack as a result of the stresses set up during the cooling appears to be less when zirconium is present.

Some typical specific examples of castings subjected in use to elevated temperatures contemplated by the present invention are valve parts including cast valve bodies, valve seats, disks, pistons, piston rings, valve stem guides, reaction vessels, stirrers, etc., operating at temperatures of 600 to 1100° F., particularly 700 to 900° F., where strength, freedom from cracking and the ability to withstand stress and sustain shock loads, etc., are required. Many of these castings are hollow, i. e., characterized by having walls defining an enclosed space, e. g., valve bodies, reaction vessels, piston rings, etc. Others, such as stirrers, may be of irregular section. These castings are used in the unworked condition, i. e., the castings are not wrought by rolling, forging, drawing or the like, although they may be and often are dressed by machining, grinding, etc. The term "unworked castings" as used herein is not to be construed as excluding castings that have been dressed.

Although the present invention has been described in connection with certain preferred embodiments thereof, modifications and variations may be resorted to as those skilled in the art will readily understand.

We claim:

1. A cast valve body adapted for high tempera-

ture application made of an alloy comprising about 25% to 35% copper, about 1 to 1.5% silicon, about 0.5% to 2% manganese, iron about 0.5% to 2.5%, carbon about 0.1% to 0.25%, about 0.03% to 0.75% zirconium, and the balance nickel.

2. An unworked casting made of an alloy comprising about 25% to 35% copper, about 3% to 5% silicon, about 0.5% to 2% manganese, about 0.5% to 5% iron, about 0.1% to 0.25% carbon, zirconium from an effective amount to about 1%, and the balance nickel.

3. As a new article of manufacture, an unworked casting made of an alloy comprising about 10% to 48% copper, about 1% to 5% silicon, about 0.04% to 0.35% carbon, about 0.5 to 5% manganese, about 0.5 to 5% iron, an effective amount up to about 1% zirconium, and the balance nickel.

4. As a new article of manufacture, an unworked casting made of an alloy comprising about 10% to 48% copper, about 1% to 5% silicon, about 0.04% to 0.35% carbon, an effective amount up to about 1% zirconium, metal selected from the group consisting of manganese and iron from about 0.5% to not more than about 5% of each, and the balance nickel.

5. As a new article of manufacture, an unworked casting made of a nickel base alloy containing about 10% to 48% copper, over 0.5% to about 5% silicon, about 0.04% to 0.6% carbon, zirconium from an effective amount to about 1%, metal selected from the group consisting of manganese and iron in an amount not exceeding about 5% of each effective to impart good casting properties to the alloy, and the balance nickel.

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