

[54] CORROSION AND WEAR RESISTANT
NICKEL ALLOY

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[22] Filed: Dec. 27, 1968

[21] Appl. No.: 787,435

[52] U.S. Cl. 75/134, 75/170, 75/171,
75/175.5

[51] Int. Cl. C22c 15/00, C22c 19/00

[58] Field of Search 75/134, 135, 170, 171, 175.5;
148/32, 32.5

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[57] ABSTRACT

Corrosion and wear resistant nickel alloys are disclosed wherein 1-50 at. % of the Ni atoms is substituted by one or more of Fe, Mo, Co and Cr and 0-10 at. % of Ti atoms is substituted by Zr. The Ni atoms and Ti atoms are contained in an alloy consisting of 45-53 at. % of Ti and the remainder of Ni.

16 Claims, 2 Drawing Figures

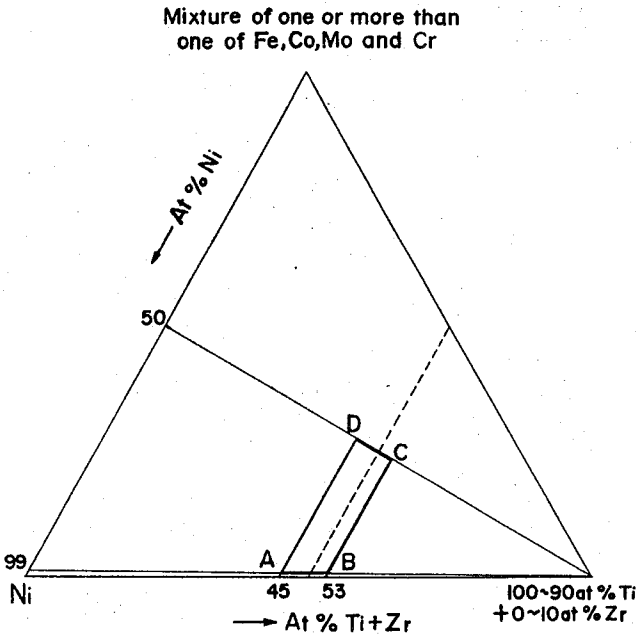


FIG-1

Mixture of one or more than
one of Fe, Co, Mo and Cr

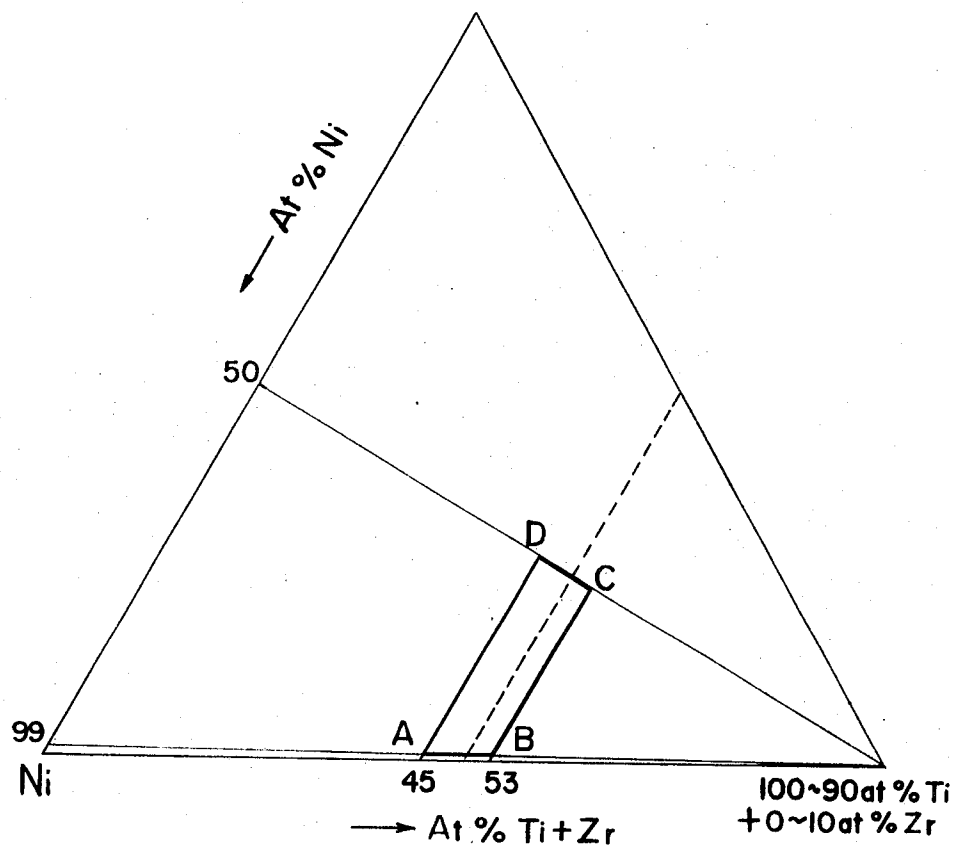
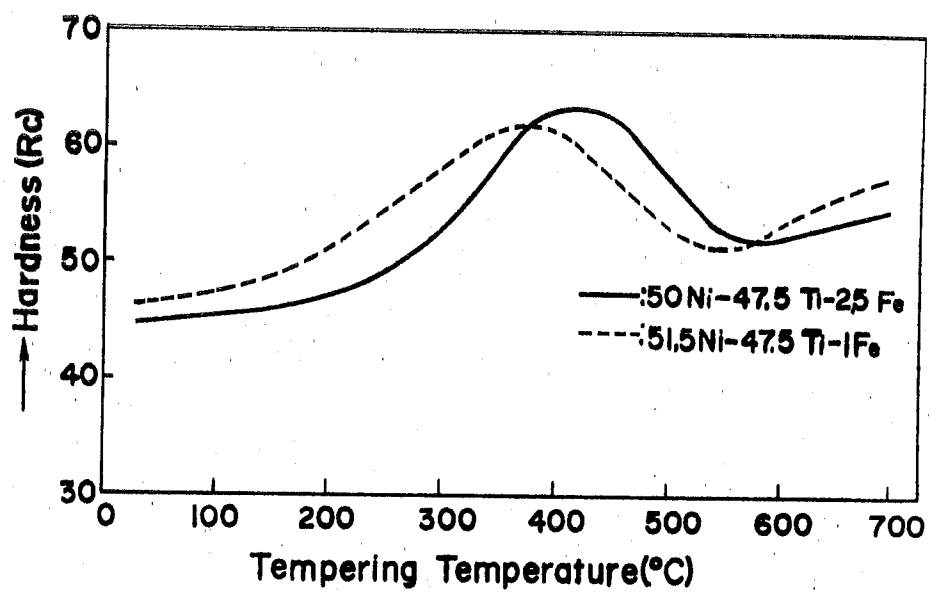


FIG-2



CORROSION AND WEAR RESISTANT NICKEL ALLOY

This invention relates to an improvement of intermetallic compound NiTi and nickel-titanium alloys of substantially the same composition as that of NiTi and particularly to Ni-Ti alloys free from transformation caused by a temperature change or by working within the practical temperature range and having a high mechanical strength at room temperature and high temperature, excellent anti-corrosive and wear resisting properties and plasticity.

The intermetallic compound NiTi and Ni-Ti alloys having substantially the same composition as that of NiTi are known to have excellent mechanical strength and vibration damping property owing to special transformation occurring at about room temperature. It is known that NiTi and Ni-Ti alloys of substantially the same construction as that of NiTi have considerable plasticity unlike any other type of intermetallic compound. In view of the above mentioned peculiar properties, NiTi and Ni-Ti alloys having substantially the same composition as that of NiTi are used for machines and apparatuses for space development, temperature sensing devices, various kinds of underwater weapons, tools, etc. However, NiTi and Ni-Ti alloys of substantially the same composition as that of NiTi have the disadvantages that they are not sufficiently resistant to some kinds of acids and have not enough mechanical strength at high temperature, that the dimensions of their product considerably vary above and below the transformation temperature which is near room temperature, and that they are transformed by working at a temperature higher than said transformation temperature and if they are heated to a temperature higher than a given temperature, said transformation returns to the original condition so that they return to the configuration prior to the working. As above mentioned, NiTi and Ni-Ti alloys of substantially the same composition as that of NiTi have a considerable plasticity unlike any other type of intermetallic compound, but their rate of reduction by rolling is limited to about 20 percent, beyond which cracks will develop therein. NiTi and Ni-Ti alloys of substantially the same composition as that of NiTi are highly active at high temperature so that it is impossible to melt them in a crucible. Thus, to manufacture product of these NiTi and Ni-Ti alloys of uniform quality they must be subjected repeatedly to complicated arc melting process in the same manner as for titanium alloys in general. Moreover, such arc melting process cannot make use of scraps of Ni or Ti or their alloys and therefore makes the manufacturing cost high. Owing to the above described defects NiTi and Ni-Ti alloys of substantially the same composition as that of NiTi have not practically been used for apparatuses and parts to be used in the chemical and mechanical industrial fields.

An object of the invention is to provide corrosion and wear resistant, high strength nickel alloys for use for general apparatus and parts for the chemical and machinery industries by preventing transformation caused by a temperature change or by working within the practical temperature range and by improving mechanical strength at room temperature and high temperature and corrosion and wear resistance.

Another object of the invention is to provide a melting and casting method in which scraps of raw materials and alloys can be used and an ingot substantially free from segregation can be produced at a low cost simply by melting in crucible.

Still another object of the invention is to provide a method of heat treating the alloy according to the invention for further improvement of mechanical strength.

The inventors have investigated on changes of the properties of NiTi and Ni-Ti alloys of substantially the same composition as that of NiTi by substituting a part of the Ni and Ti atoms by various kinds of elements and found out that substitution of 1-50 at. % of Ni atom contained in an alloy consisting of 45-53 at. % of Ti and the remainder of Ni by one or more of Fe, Mo, Co and Cr (hereinafter called "M") has yielded the surprising result that transformation caused by temperature change or by working within the practical temperature range can be prevented and mechanical strength at

room temperature and high temperature and corrosion and wear resistance can be improved. The inventors have also found out that substitution of 1-50 at. % of the Ni atoms by M and substitution of 0-10 at. % of Ti atoms by Zr yielded the result that the above mentioned mechanical strength at room temperature and high temperature and corrosion resistance can further be improved.

Other objects, features and advantages of the invention will become apparent from the following specification, in conjunction with the accompanying drawings in which:

FIG. 1 is a ternary phase diagram; and

FIG. 2 shows curves illustrating the relation between tempering temperature and hardness of the alloys according to the invention.

The range of the compositions of the alloys according to the invention will now be explained with reference to FIG. 1 showing a ternary phase diagram where

Point A ((Ti+Zr) 45 at. %, M 0.55 at. % and the remainder Ni),

Point B ((Ti+Zr) 53 at. %, M 0.47 at. % and the remainder Ni),

Point C ((Ti+Zr) 53 at. %, M 23.5 at. % and the remainder Ni),

Point D ((Ti+Zr) 45 at. %, M 27.5 at. % and the remainder Ni)

are connected in the order of A, B, C, and D with straight lines to form a quadrilateral within which lies the compositions of the alloys according to the invention, and (Ti+Zr) designates a composition in which 0-10 at. % of the Ti atoms is substituted by Zr.

The reason why 1-50 at. % of Ni atoms contained in the alloys according to the invention consisting of 45-53 at. % of Ti and the remainder of Ni is substituted by M (the atomic ratio of Ni:M lies within a range of 99:1-50:50) is that in the ternary phase diagram shown in FIG. 1 a brittle and injurious intermetallic compound Ni_3Ti precipitates as a second phase in the range below the line AD (less than 45 at. % of (Ti+Zr)), while in the range above the line BC (more than 53 at. % of (Ti+Zr)) a brittle and injurious intermetallic compound NiTi_2 precipitates as a second phase, so that the plasticity inherent to NiTi and Ni-Ti alloys of substantially the same composition as that of NiTi decreases and hot and cold working becomes considerably difficult. In the range below the line AB ((Ti+Zr) 45-53 at. %, the remainder (Ni+M) whose atomic ratio is 99:1) the advantageous effect of substitution of a part of Ni atoms by M decreases, while in the range above the line CD ((Ti+Zr) 45-53 at. %, the remainder (Ni+M) whose atomic ratio is 50:50), the properties of NiTi deteriorate, thus considerably decreasing the plasticity thereof and making the hot and cold working difficult.

In the alloys according to the invention M for substituting a part of the Ni atoms is Fe, Mo, Co and Cr. All these elements give the above mentioned advantageous effects. Especially, Mo and Co give an excellent corrosion resistance against H_2SO_4 . Co gives the most excellent corrosion resistance against HDI, Cr gives the most excellent wear resistance, followed by Mo, Co and Fe in the order given. Fe is most effective in preventing transformation caused by a temperature change or by working within the practical temperature range, followed by Mo, Co and Cr in the order given. For improvement of mechanical strength Mo is most effective. Thus, through proper selection of Fe, Mo, Co, and Cr, it is possible to obtain alloys having excellent properties, good for intended purposes.

The reason why 0-10 at. % of Ti atoms of the alloys according to the invention is substituted by Zr is that said substitution of the Ti atoms by Zr renders it possible to further improve the mechanical strength of the alloy according to the invention at room temperature and high temperature and also the corrosion resistance against HCl, although the substitution of 1-50 at. % of the Ni atoms by M is capable of satisfactorily obtaining the object of the invention without substituting a part of Ti atoms by Zr. Substitution of a part of Ti atoms by Zr tends to

decrease the plasticity of the alloys according to the invention. If the rate of substitution of Ti atoms by Zr is made larger than the atomic ratio of 9:1, the plasticity of the alloys according to the invention decreases, with the result that the hot and cold working cannot be carried out.

As above mentioned, substitutions, according to the invention, of 1-50 at. % of the Ni atoms by M and of 0-10 at. % of the Ti atoms by Zr in the alloy consisting of 45-53 at. % of Ti and the remainder of Ni make it possible to prevent transformation caused by temperature change or by working within the practical temperature range, improve the mechanical strength at room temperature and high temperature, and further improve the corrosion and wear resistance of the alloys. In order to obtain alloys having improved hot and cold workability, it is desirable to substitute by M 1-25 at. % of the Ni atoms of alloys consisting of 47-52 at. % of Ti and the remainder of Ni. It is more desirable to substitute by M 1-20 at. % of the Ni atoms of the alloys consisting of 48-52 at. % of Ti and the remainder of Ni. In order to obtain alloys according to the invention having excellent hot and cold workability and mechanical strength, 0.1-7 at. % of the Ti atoms may be substituted by Zr.

In order to obtain alloys according to the invention having particularly excellent hot and cold workability 2-20 at. % of the Ni atoms of alloys consisting of 49.5-50.5 at. % of Ti and the remainder of Ni may be substituted by M. Moreover, in order to obtain alloys according to the invention having excellent mechanical strength and corrosion resistance, 1-20 at. % of the Ni atoms of alloys consisting of 50.7-52.0 at. % of Ti and the remainder of Ni may be substituted by M and 0.1-5 at. % of the Ti atoms may be substituted by Zr. Furthermore, in order to obtain alloys which will have improved mechanical strength when quenched and tempered, 1-20 at. % of the Ni atoms of alloys consisting of 48-49 at. % of Ti and the remainder of Ni may be substituted by M. Moreover, in order to obtain alloys which will have more improved mechanical strength when quenched and tempered, 1-5 at. % of the Ni atoms of alloys consisting of 48-48.6 at. % of Ti and the remainder of Ni may be substituted by M.

As above mentioned, it is possible to obtain alloys having the above mentioned properties by substituting by M a part of the Ni atoms of NiTi and Ni-Ti alloys of substantially the same composition as that of NiTi and further it is possible to obtain alloys having an excellent corrosion resistance against hydrochloric acid and sulfuric acid by using Mo or Co as M and substituting a part of the Ti atoms by Zr. It is more desirable to use a combination of Mo and Co as M. In order to obtain alloys having particularly excellent wear resistance it is desirable to use Cr or Mo as M. It is more desirable to use a combination of Mo and Cr as M. In order to obtain alloys having an excellent cold workability it is desirable to use Fe, Mo or Co as M. It is more desirable to use a combination of Fe and Mo or of Mo and Co as M. In order to obtain alloys having an excellent mechanical strength at room temperature and high temperature, it is desirable to use Mo or Cr as M and or substitute a part of the Ti atoms by Zr. It is more desirable to use a combination of Mo and Cr as M and or substitute a part of the Ti atoms by Zr. In order to obtain alloys having excellent corrosion resistance and cold workability, it is desirable to substitute a part of the Ni atoms by Fe, Mo and Co, preferably at an atomic ratio of 1:1:1. In order to obtain alloys having an excellent corrosion resistance and a more improved cold workability, it is desirable to substitute a part of the Ni atoms by Fe and Mo as M, preferably at an atomic ratio of 3:2. In order to obtain alloys having the most excellent corrosion resistance and cold workability, it is desirable to substitute a part of the Ni atoms by Mo and Co as M, preferably at an atomic ratio of 2:3. In order to obtain alloys having a particularly excellent wear resistance, it is desirable to substitute a part of the Ni atoms by Cr and Mo as M, preferably at an atomic ratio of 1:1. In order to obtain alloys having the most excellent wear resistance, it is desirable to substitute a part of the Ni atoms by Cr as M.

As above mentioned, the alloys according to the invention contain Ni atoms part of which are substituted by M. If Fe and Cr which are cheaper than Ni are used as M, the alloys according to the invention are considerably less expensive.

The alloys according to the invention may contain as impurities less than 0.1 percent by weight of Cu, less than 0.01 percent by weight of P, less than 0.55 percent by weight of Mn, less than 0.6 percent by weight of C, less than 0.55 percent by weight of S, less than 0.11 percent by weight of Si, less than 0.5 percent by weight of Mg, less than 0.14 percent by weight of Al, less than 0.7 percent by weight of V, and less than 0.13 percent by weight of Ti without giving much adverse effect on the properties of the alloys according to the invention.

The alloys according to the invention may be melted by high frequency heating process in a crucible made of graphite or carbon under vacuum or in the atmosphere of inert gases such as argon, helium, etc.

Heretofore, NiTi and Ni-Ti alloys of substantially the same composition as that of NiTi have been melted by arc melting process using consumable or non-consumable electrodes and subsequently casted in a water cooled mold made of copper under vacuum or in the inert gas atmosphere as in the case of general titanium alloys. Such conventional method is complex in operation. According to this method, the raw material is melted little by little locally by electric arc and is not therefore thoroughly melted and blended, so that such electric arc melting must be repeated several times to obtain ingots of uniform composition. This makes melting and casting costly. Moreover, if Mo having a high melting point is used as M, it is impossible to melt it thoroughly and therefore Mo must be used in the form of a mother alloy.

Under the above circumstances, the inventors have investigated on various methods of melting and casting NiTi and Ni-Ti alloys of substantially the same composition as that of NiTi and found out a method which comprises substituting a part of the Ni atoms by M, charging metal compositions into a graphite or carbon crucible in close contact with one another, and melting said metal compositions by a high frequency heating process at a temperature higher than the melting point of alloys under the present invention but less than 1,700° C under vacuum or in the inert gas atmosphere, thereby obtaining a uniform ingot without substantially any reaction of the molten bath with the crucible.

A crucible made of oxides such as alumina, silica, magnesia, etc., other than graphite or carbon, causes the molten alloy to react intensely with it. The melting requires a long time unless the metal compositions are brought into close contact with one another in the crucible, thus resulting in an increase of the carbon content in the alloy. Moreover, if the temperature rises higher than 1,700° C, the molten alloy intensely reacts with the crucible, with the resultant increase in carbon content in the alloy.

The alloys according to the invention consisting of less than 50 at. % of (Ti+Zr) and the remainder of Ni, in which part of the Ni atoms are substituted by M, have improved mechanical strength when quenched and tempered.

That is, the alloys having the above mentioned compositions are heated at a temperature of 700°-1,000° C and then immediately quenched into water or oil and then tempered at a temperature of 250°-450° C. In this way their mechanical strength can be increased considerably.

Alloys quenched at a temperature less than 700° C do not show any sufficient hardening phenomenon, while alloys heated at a temperature higher than 1,000° C are excessively oxidized. The tempering at a temperature less than 250° C or higher than 450° C would not improve the mechanical strength. In order to improve the mechanical strength by quenching and tempering processes, it is desirable to substitute by M 1-20 at. % of the Ni atoms of the alloys consisting of 48-49 at. % of Ti and the remainder of Ni. It is most desirable to substitute by M 1-5 at. % of the Ni atoms of the alloy consisting of 48-48.6 at. % of Ti and the remainder of Ni.

The invention will now be described with reference to examples.

EXAMPLE 1

The alloys according to the invention having compositions shown in the following Tables 1 and 2 were casted by heating and melting them in graphite crucible at a temperature of about 1,410° C by a high frequency heating process under vacuum. These alloys were formed into sheets, each having a thickness of 1.5 mm by hot press-hammer-rolling processes at a temperature of 930°-700° C and the oxidized scales were removed by a shot blast and then the thus treated sheets were pickled in an aqueous solution of nitric acid-hydrofluoric acid. Then, the sheets were immersed into various chemicals to determine the rate of corrosion from the weight variation in a given time. The results are shown in Tables 1 and 2. For comparison, NiTi and Ni-Ti alloys of substantially the same composition as that of NiTi were casted by arc melting process repeated five times in argon atmosphere by the use of consumable electrodes, and the alloys thus obtained were formed into sheets each having a thickness of 1.7 mm by hot press-hammer-rolling processes at a temperature of 930° to 700°C and then the oxidized scales were removed by a shot blast and the thus treated sheets were pickled in an aqueous solution of nitric acid-hydrofluoric acid. The corrosion rate of these sheets was determined and the results are also shown in Tables 1 and 2.

Table 1 shows the corrosion rate of the sheets immersed in 5 wt% and 10 wt% aqueous solutions of sulfuric acid at 100° C for 24 hours and Table 2 shows the corrosion rate of the sheets immersed in 3 wt% and 5 wt% aqueous solutions of hydrochloric acid at 100° C for 24 hours.

TABLE 1

Alloy	Composition (at percent)							Corrosion rate (μ /day)	
	Ni	Fe	Mo	Co	Cr	Ti	Zr	5 wt. per- cent H ₂ SO ₄	10 wt. per- cent H ₂ SO ₄
Conventional alloys.....	50	-----	-----	-----	-----	50	-----	423	817
	53	-----	-----	-----	-----	47	-----	571	992
	48	-----	-----	-----	-----	52	-----	540	924
Alloys according to the invention.....	45	5	-----	-----	-----	50	-----	366	775
	40	10	-----	-----	-----	50	-----	401	800
	49.7	-----	0.3	-----	-----	50	-----	63	133
	45	-----	5	-----	-----	50	-----	5	14
	42	-----	8	-----	-----	50	-----	3	6
	40	-----	10	-----	-----	50	-----	3	7
	49	-----	-----	1	-----	50	-----	27.8	560
	45	-----	-----	5	-----	50	-----	16.5	316
	40	-----	-----	10	-----	50	-----	118	247
	35	-----	-----	15	-----	50	-----	105	226
	45	-----	-----	-----	5	50	-----	332	739
	40	-----	-----	-----	10	50	-----	342	761
	40	5	5	-----	-----	50	-----	6	13
	45	-----	5	-----	-----	45	5	7	15
	48	-----	5	-----	-----	47	-----	104	207
	43	-----	5	-----	-----	52	-----	82	171
	48	-----	-----	5	-----	47	-----	195	380
	43	-----	-----	5	-----	52	-----	180	362
	47.5	1.5	1	-----	-----	50	-----	18	35
	47.5	-----	1	1.5	-----	50	-----	14	29
	47	1	1	1	-----	50	-----	19	36
	40	-----	5	5	-----	50	-----	3	5

TABLE 2

Alloy	Composition (at percent)							Corrosion rate (μ /day)	
	Ni	Fe	Mo	Co	Cr	Ti	Zr	3 wt. per- cent HCl	5 wt. per- cent HCl
Conventional alloys.....	50	-----	-----	-----	-----	50	-----	11	130
	53	-----	-----	-----	-----	47	-----	12	145
	48	-----	-----	-----	-----	52	-----	11	141
Alloy3 according to the invention.....	45	5	-----	-----	-----	50	-----	9	119
	40	10	-----	-----	-----	50	-----	9	112
	45	-----	5	-----	-----	50	-----	8	98
	40	-----	10	-----	-----	50	-----	8	86
	49.8	-----	-----	0.2	-----	50	-----	9	116
	49.6	-----	-----	0.4	-----	50	-----	8	15
	45	-----	-----	5	-----	50	-----	4	9
	40	-----	-----	10	-----	50	-----	2	5
	35	-----	-----	15	-----	50	-----	2	4
	45	-----	-----	-----	5	50	-----	9	115
	40	-----	-----	-----	10	50	-----	7	96
	45	-----	-----	5	-----	49.5	0.5	4	8
	45	-----	-----	5	-----	48.5	1.5	3	7
	45	-----	-----	5	-----	47.5	2.5	1	2
	45	-----	-----	5	-----	45	-----	1	2
	48	-----	-----	5	-----	47	-----	6	11
	43	-----	-----	5	-----	52	-----	5	10
	48	-----	-----	5	-----	45.5	1.5	4	8
	43	-----	-----	5	-----	50.5	1.5	4	7
	47.5	1.5	1	-----	-----	50	-----	9	113
	47.5	-----	1	1.5	-----	50	-----	8	12
	47	1	1	1	-----	50	-----	9	13
	40	-----	5	5	-----	50	-----	2	4

As seen from Table 1, against the aqueous solutions of sulfuric acid, the alloys in which nickel atoms are partially substituted by M and those in which nickel atoms are partially substituted by M and further titanium atoms are partially substituted by zirconium, have considerably improved corrosion resistance and of them, the alloys, in which nickel atoms are partially substituted by Mo or Co, are excellent in corrosion resistance, and particularly the alloys, in which nickel atoms are partially substituted by both of Mo and Co, have the highest corrosion resistance.

As regards the relation between the rate of substitution and its effect on improvement of corrosion resistance, Mo is fairly effective in improving the corrosion resistance even when used at a substitution rate of as low as 0.3 at. % (atomic ratio of Ni and Mo is 99.7:0.3) and the effect increases until the substitution rate reaches about 8 at. %, but beyond such a rate, the effect becomes constant. In the case of cobalt, the area developing the effect lies in a higher side of the rate of substitution than that of molybdenum.

Furthermore, as seen from Table 2, against the aqueous solutions of hydro-chloric acid, the alloys in which Ni atoms are partially substituted by M and those in which Ni atoms are partially substituted by M and further titanium atoms are partially substituted by zirconium, have considerably improved corrosion resistance. Among M, cobalt or a combination of Co and Mo is the most effective.

As regards the relation between the rate of substitution and its effect on improvement of corrosion resistance, in the case of cobalt, the effect appears when the rate of substitution is

about 0.4 at. % (atomic ratio of Ni to Co being 99.6:0.4) and increases until the rate reaches about 10 at. %, but beyond such a rate, the effect remains constant. Furthermore, in case titanium atoms are partially substituted by Zr the effect appears when the rate of substitution is about 1.0 at. % (atomic ratio of Ti to Zr being 99:1) and increases until the rate reaches about 5 at. %; but, beyond such a rate, the effect remains substantially constant.

EXAMPLE 2

Sheets, 1.5 mm thick, made of the alloys according to the invention in the same manner as described in Example 1 and sheets of the same thickness made of conventional alloys the compositions of both alloys being shown in Table 3, were polished with an emery paper and then buffed and thereafter subjected to abrasion test by Ohgoshi's rapid abrasion tester which will be described below, to determine the coefficient of wear and the thus obtained results are shown in Table 3.

The above mentioned test was effected as follows:

The above described sheet was set in parallel with the axis of a friction disc having a diameter of about 30 mm and a thickness of about 3 mm and the friction disc was pressed against the surface of the above described sheet under various pressures and rotated at various speeds at fixed points on the sheet until it covers a given running distance (circumference of the disc X number of rotations) and the width of the scratch marks were measured and the coefficient of wear (Ws) was calculated according to the following formula

$$Ws = Bv_0^3/8rP_0l_0$$

Ws = Coefficient wear

$$B = 3.05$$

b_0 = Width of scratch mark

r = Radius of the friction disc

P_0 = Pressure of applying disc against the sample sheet

l_0 = Running distance

In this example, r was 30 mm, P_0 , 6.5 Kg; and l_0 , 200 m.

speed of the disc is low, at whatever rate of the substituting elements may be used. But, in the field of "bright-surface wear" (wearing in which worn metal surface is bright and the coefficient of wear sharply increases as rotating speed increases) where the rotating speed is high, improvement of wear resistance is seen when the rate of substitution is about 0.5 at. %. The coefficient of wear decreases according to increase in the rate of substitution up to 30 at. %.

Further, in this test, as the rotating speed increases, the temperature on the wearing surface rises and hence the above described test result shows that the temperature at which the oxidated wear changes to the bright-surface wear shifts to the higher temperature side by partial substitution of Ni atom by M and Ti atom by Zr.

EXAMPLE 3

Sheets, about 5 mm thick, made of the alloys according to the invention in the same manner as that described in the Example 1 and sheets of the same thickness made of conventional alloys, the compositions of both alloys being as shown in Table 4 and manufactured were finally tempered in argon atmosphere at 930° C for 1 hour and then cooled to room temperature at a cooling rate of about 50° C in every hour. Measurement was taken of the hardness at room temperature and a high temperature of 700° C, the hardness at room temperature after the quenching and tempering processes (tempering at 350° C for 1 hour after quenching in water from 930° C), the temperature at which the transformation occurs (hereinafter expressed as "Ms") and the maximum temperature beyond which the transformation is no longer caused by working (Md) (hereinafter expressed as "Md"). The results are shown in Table 4.

Ms in Table 4 was determined by sound when the sample sheet was struck by hammer, because conventional NiTi and Ni-Ti alloys of substantially the same composition as that of NiTi vary discontinuously and remarkably in the vibration

TABLE 3

Alloy	Composition (at percent)							Coefficient of wear (mm. ² /kg.)	
	Ni	Fe	Mo	Co	Cr	Ti	Zr	Rotating speed 1.4 m./sec.	Rotating speed 3.6 m./sec.
Conventional alloys.....	50	-----	-----	-----	50	-----	-----	2.6×10 ⁻⁸	79×10 ⁻⁸
	53	-----	-----	-----	47	-----	-----	2.2×10 ⁻⁸	72×10 ⁻⁸
	48	-----	-----	-----	52	-----	-----	2.4×10 ⁻⁸	73×10 ⁻⁸
Alloys according to the invention.....	45	5	-----	-----	50	-----	-----	2.3×10 ⁻⁸	68×10 ⁻⁸
	40	10	-----	-----	50	-----	-----	2.2×10 ⁻⁸	60×10 ⁻⁸
	49.5	-----	0.5	-----	50	-----	-----	2.3×10 ⁻⁸	58×10 ⁻⁸
	45	-----	5	-----	50	-----	-----	2.0×10 ⁻⁸	22×10 ⁻⁸
	40	-----	10	-----	50	-----	-----	2.2×10 ⁻⁸	10×10 ⁻⁸
	35	-----	15	-----	50	-----	-----	1.9×10 ⁻⁸	7×10 ⁻⁸
	45	-----	-----	5	50	-----	-----	2.1×10 ⁻⁸	19×10 ⁻⁸
	40	-----	-----	10	50	-----	-----	2.0×10 ⁻⁸	11×10 ⁻⁸
	49	-----	-----	-----	1	50	-----	2.0×10 ⁻⁸	54×10 ⁻⁸
	45	-----	-----	-----	5	50	-----	2.2×10 ⁻⁸	15×10 ⁻⁸
	40	-----	-----	10	50	-----	-----	1.8×10 ⁻⁸	7×10 ⁻⁸
	35	-----	-----	15	50	-----	-----	1.7×10 ⁻⁸	5×10 ⁻⁸
	45	-----	-----	5	49	1	-----	2.5×10 ⁻⁸	14×10 ⁻⁸
	45	-----	-----	5	45	5	-----	2.5×10 ⁻⁸	12×10 ⁻⁸
	48	-----	-----	5	47	-----	-----	2.0×10 ⁻⁸	13×10 ⁻⁸
	43	-----	-----	5	52	-----	-----	2.3×10 ⁻⁸	16×10 ⁻⁸
	47.5	1.5	1	-----	50	-----	-----	2.2×10 ⁻⁸	31×10 ⁻⁸
	47.5	-----	1	1.5	50	-----	-----	2.1×10 ⁻⁸	15×10 ⁻⁸
	48	-----	1	-----	1	50	-----	2.0×10 ⁻⁸	24×10 ⁻⁸
	48	-----	-----	2	50	-----	-----	1.9×10 ⁻⁸	23×10 ⁻⁸
	40	-----	5	-----	5	50	-----	1.8×10 ⁻⁸	9×10 ⁻⁸

As seen from Table 3, the wear resistance is not considerably influenced by the atomic ratio of (Ni+M) and (Ti+Cr) and as the rate of substitution of M and Zr increases, the rate of increase in wear along with increase in rotating speed of the disc is reduced. Furthermore, the influence of each substituting element is most remarkable in Cr and the effect decreases in the order of Mo, Co, Fe and Zr and the best result is obtained in the use of a combination of Cr and Mo. Irrespective of the kind of element used for substitution, the wear resistance of alloys is scarcely improved in the field of "oxidated wear" (wearing in which worn metal surface is covered with metallic oxide and the coefficient of wear is very low, irrespective of the rotating speed) where the rotating

damping property above and below the transformation temperature and when the alloys are struck at a temperature higher than the transformation temperature, a metallic sound is given out, while is struck at a temperature lower than said transformation temperature, the alloys make a non-metallic dull sound.

Md in Table 4 was defined as follows:

If the alloy sheet once deformed at a temperature lower than Md returns to its original shape when heated to a temperature higher than a specific temperature. In consideration of such property, Md is defined as the maximum bending temperature above which the bent sheet cannot return to its original form when heated at 500° C.

TABLE 4

Alloy	Composition (at percent)							Ms (° C.)	Md (°C.)	Hardness ¹	Hardness ²	Hardness at 700° C. (HV)
	Ni	Fe	Mo	Co	Cr	Ti	Zr					
Conventional alloys.....	50					50		65	>300	4	4	35
Alloys according to the invention.....	45	5				50		Ms<-196	Md<-196	9	10	45
	40	10				50		Ms<-196	Md<-196	20	22	53
	35	15				50		Ms<-196	Md<-196	27	27	58
	48		2			50		-196<Ms	-72<Md	31	35	50
	45		5			50		<-72	<-0	40	43	86
	40		10			50		Ms<-196	Md<-196	45	44	124
	45			5		50		-196<Ms	-196<Md	8	8	43
	35			15		50		<-72		23	24	56
	40				10	50		Ms<-196	Md<-196	29	26	45
	47.5	1.5	1			50		Ms<-196	Md<-196	28	30	53
	47.5		1	1.5		50		Ms<-196	Md<-196	28	27	51
	45	5				45	5	-196<Ms		21	19	72
	46.4	5.1				48.5		<-72		38	56	73
	47.5	5.3				47		Ms<-196	Md<-193	35	61	92
	49.5	5.5				45		Ms<-196	Md<-196	37	64	109
	47.7			5.3		47		Ms<-196	Md<-196	36	59	91
	47.7				5.3	47		-196<Ms		52	50	88
	47.7	2.65			2.65	47		<-72	-196<Md	44	54	90
	47.7			2.65	2.65	47		Ms<-196	-196<Md	45	54	90
	43.2	4.8				52		Ms<-196	-196<Md	22	24	74
	46.4			5.1		48.5		Ms<-196	Md<-196	37	55	70
	49.0	1.5	1.0			48.5		Ms<-196	Md<-196	53	65	79
	40		5		5	45	5	Ms<-196	Md<-196	55	57	131

¹ At room temperature after tempering (IIRC).

² At room temperature after quenching and tempering (IIRC).

As seen from Table 4, the alloys according to the invention in which Ni atoms are partially substituted by M and Ti atoms by zirconium are extremely lower in Ms and Md than the conventional alloys.

The effect of decreasing Ms and Md is most remarkable in Fe among M and the effect reduces in the order of Mo, Co and Cr.

The hardness in the annealed state and the hardness at high temperature of the alloys, wherein Ni atoms are partially substituted by M and Ti atoms by zirconium, are improved highly and as to the substituted element, Mo has the most remarkable

EXAMPLE 4

The alloys according to the invention manufactured by the method similar to that described in Example 1 and the conventional alloys were formed into sheets each having a thickness of 2 mm. The sheets thus obtained were finally annealed at 93° C in argon atmosphere for one hour.

Then, these sheets were cooled at a cooling rate of about 50° C/min to room temperature and then subjected to cold rolling. The maximum rate of rolling beyond which further rolling is impossible owing to crack formation was measured and the results thus obtained are shown in Table 5.

TABLE 5

Alloy	Compositions (at percent)							Maximum rate of rolling (percent)
	Ni	Fe	Mo	Co	Cr	Ti	Zr	
Conventional alloys.....	50					50		22
	52					48		10
	48					52		8
Alloys according to the invention.....	47.5	2.5				50		33
	45	5				50		30
	49		1			50		32
	47.5		2.5			50		28
	47.5			2.5				34
	45				5			30
	47.5				2.5			25
	47.5	1.5	1			50		37
	47.5		1	1.5		50		39
	47.5	2.5				47.5	2.5	23
	47	1	1	1		50		36

effect and Zr and Cr follow Mo, and Co have relatively low effect. The highest effect can be attained by a combination of Mo, Cr and Zr.

Substitution of Ni atoms by one or more of Fe, Co and Cr as M shows a remarkable age-hardening effect by quenching and tempering treatments when (Ti+Zr) atoms are less than 50 at. %. Such an effect is most remarkable when the substitution is effected by Fe.

FIG. 2 shows a relation between tempering temperature and the hardness after tempering of the alloys, wherein Ni atoms are partially substituted by Fe, at different rates of substitution.

As seen from FIG. 2 the alloy having a higher rate of substitution is larger in the hardness increase owing to the tempering, and the peak of tempering hardness shifts somewhat to the higher temperature side.

As can be seen from Table 5, the alloy according to the invention in which a part of the Ni atom content are substituted by M can have improved plasticity at about room temperature.

Heretofore, in order to improve the mechanical properties of NiTi and Ni-Ti alloys substantially the same composition as that of NiTi, addition of the third and the fourth elements thereto has been tried. But, in both cases the plasticity of the alloy becomes decreased, with the result that the hot and cold working processes become difficult thus resulting in difficulty in the practical use of the alloy. The invention provides a method of substitution by, instead of addition of, the above mentioned elements and hence can improve the mechanical properties of the alloy without decreasing its plasticity.

With regard to the effect of the elements for substituting a part of the Ni atoms of the alloy according to the invention,

Co and Fe are most effective while Mo is less effective and Cr is the least effective. Use of more than one of such elements is also effective. Particularly, the combinations of Co and Mo and the Fe and Mo are considerably effective.

EXAMPLE 5

An alloy according to the invention, in which 5 at. % of Ni atoms of NiTi were substituted by Mo and 5 at. % of the Ti atoms were substituted by Zr, was melted in a crucible made of graphite by a high frequency heating process under vacuum.

The molten alloy thus obtained was maintained at various temperatures for 20 minutes and then cast into a water cooled mold made of copper. The carbon contents of the ingots thus obtained were investigated and the results obtained are shown in Table 6.

Ni, Ti, Fe, Mo and Zr were so charged into the crucible that these elements become laminated therein so as to easily react each other.

Table 6

Melting temperature (°C)	C (%)	Melting temperature (°C)	C (%)
1,280	0.04	1,500	0.08
1,320	0.05	1,550	0.10
1,360	0.05	1,600	0.13
1,410	0.06	1,650	0.19
1,450	0.08		

As seen from Table 6, the alloys according to the invention do not react with the crucible when the temperature is less than 1,700° C so that the molten alloy is not contaminated with graphite. The alloys can therefore be used in practice.

The segregation of the alloy compositions of the ingots cast by the above mentioned method was measured and the results are shown in Table 7.

In this case, the temperature of the molten bath was 1,410° C. The results obtained by measuring the segregation of the alloys melted by the conventional arc melting process are also shown in Table 7 for the comparison.

TABLE 7

Melting method	Compositions (wt. percent)				Values of analysis (wt. percent)									
					Top of ingot					Bottom of ingot				
	Ni	Mo	Ti	Zr	Ni	Mo	Ti	Zr	C	Ni	Mo	Ti	Zr	C
Are melting:														
Once.....	47.89	8.70	43.41	40.8	6.9	43.1	45.1	10.5	44.0					
Three times.....	47.89	8.70	43.41	48.3	7.2	44.2	46.9	9.8	43.0					
Once.....	46.08	8.37	37.60	46.9	9.6	36.6	6.8	44.7	7.7	38.5	8.9			
Three times.....	46.08	8.37	37.60	46.7	8.8	37.0	7.4	46.0	8.9	37.4	7.4			
Method according to the invention.....	47.89	8.70	43.41	47.9	8.6	43.3	0.07	48.1	8.7	43.2				0.05
Do.....	46.08	8.37	37.60	46.2	8.4	37.4	7.8	0.05	46.0	8.4	37.4	8.1		0.06

As seen from Table 7, the alloy according to the invention can be melted and cast in the crucible made of graphite by means of the high frequency heating under vacuum. This casting process, given only once, provides an ingot having less segregation and carbon contamination.

The description and examples given above are intended to illustrate the best mode of performing the invention. It is apparent that many modifications thereof may occur to those skilled in the art, which will fall within the scope of the following claims.

What is claimed is:

1. A corrosion and wear resistant nickel alloy produced by replacing 1-50 at. % of the nickel atoms of intermetallic compound Ni-Ti alloy consisting essentially of 45-53 at. % titanium and the remainder Ni by a metal selected from the group consisting of Mo and Cr; and by replacing 0-10 at. % of the Ti atoms of said Ni-Ti alloy by Zr, said alloy having excellent cor-

rosion and wear resistance and a high mechanical strength at high temperature and room temperature and being hot- and cold-workable and free from transformation caused by temperature or by working within the practical temperature range.

2. The corrosion and wear resistant nickel alloy of claim 1, consisting of 47-52 at. % of Ti and the remainder of Ni, 1-25 at. % of Ni atoms being substituted by a metal selected from the group consisting of Mo and Cr, said alloy being easy to hot- and cold-work.

3. The corrosion and wear resistant nickel alloy of claim 1, consisting of 48-52 at. % of Ti and the remainder of Ni, 1-20 at. % of Ni atoms being substituted by a metal selected from the group consisting of Mo and Cr, said alloy being easier to hot- and cold-work than the nickel alloy of claim 2.

4. The corrosion and wear resistant nickel alloy of claim 1, wherein 0.1-7 at. % of Ti atoms are substituted by Zr, said alloy having a high mechanical strength.

5. The corrosion and wear resistant nickel alloy of claim 1, consisting of 49.5-50.5 at. % of Ti and the remainder of Ni, 2-20 at. % of Ni atoms being substituted by a metal selected from the group consisting of Mo and Cr, said alloy having excellent corrosion resistance and being particularly easy to hot- and cold-work.

6. The corrosion and wear resistant nickel alloy of claim 1, consisting of 50.7-52 at. % of Ti and the remainder of Ni, 1-20 at. % of Ni atoms being substituted by a metal selected from the group consisting of Mo and Cr, and 0.1-5 at. % of Ti atoms are substituted by Zr, said alloy having a high mechanical strength and excellent corrosion resistance and being easy to hot- and cold-work.

7. The corrosion and wear resistant nickel alloy of claim 1, consisting of 48-49 at. % of Ti and the remainder of Ni, 1-20 at. % of Ni atoms being substituted by a metal selected from the group consisting of Mo and Cr, said alloy being capable of improving its mechanical strength by means of quenching and tempering processes.

8. The corrosion and wear resistant nickel alloy of claim 1, consisting of 48-48.6 at. % of Ti and the remainder of Ni, 1-5 at. % of Ni atoms being substituted by a metal selected from the group consisting of Mo and Cr, said alloy being capable of further improving its mechanical strength by means of quenching and tempering processes.

9. The corrosion and wear resistant nickel alloy of claim 1,

wherein 1-50 at. % of the nickel atoms are replaced by Mo only and 5-95 at. % of said replacing Mo atoms are replaced by at least one of Fe and Co, said alloy having excellent corrosion resistance and cold workability.

10. The corrosion and wear resistant nickel alloy of claim 9, wherein said replacing Mo atoms are replaced by Fe and Co such that Mo, Fe and Co have an atomic ratio of 1:1:1.

11. The corrosion and wear resistant alloy of claim 1, wherein 1-50 at. % of the nickel atoms are replaced by Mo only and 5-95 at. % of said replacing Mo atoms are replaced by Fe only, said alloy having excellent corrosion resistance and cold workability.

12. The corrosion and wear resistant alloy of claim 11, wherein said replacing Mo atoms are replaced by Fe such that Mo and Fe have an atomic ratio of 2:3.

13. The corrosion and wear resistant nickel alloy of claim 1, wherein 1-50 at. % of the nickel atoms are replaced by Mo

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only and 5-95 at. % of said replacing Mo atoms are replaced by Co, said alloy having the most excellent corrosion resistance and cold workability.

14. The corrosion and wear resistant nickel alloy of claim 13, wherein the atomic ratio between Mo and Co is 2:3.

15. The corrosion and wear resistant nickel alloy of claim 1,

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wherein 1-50 at. % of the nickel atoms are replaced by Mo and Cr whose atomic ratio is 1:1.

16. The corrosion and wear resistant nickel alloy of claim 1, wherein 1-50 at. % of the nickel atoms are replaced by Cr only, said alloy having the most excellent wear resistance.

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