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(54) **HIGH TEMPERATURE SHAPE MEMORY ALLOY, ACTUATOR AND MOTOR**

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(57) **ABSTRACT**

A high temperature shape memory alloy is provided which possesses high machinability and is suitable for high temperature applications. The high temperature shape memory alloy consists of Ni from 34.7 mol % to 48.5 mol %, at least either Zirconium or Hafnium as transformation temperature increasing additives, with the sum of which 6.8 mol % to 22.5 mol %, and at least either Niobium or Tantalum as machinability improving additives, with the sum of which 1 mol % to 30 mol %; and Boron less than 2 mol %; and Titanium as the balance; and unavoidable impurity.

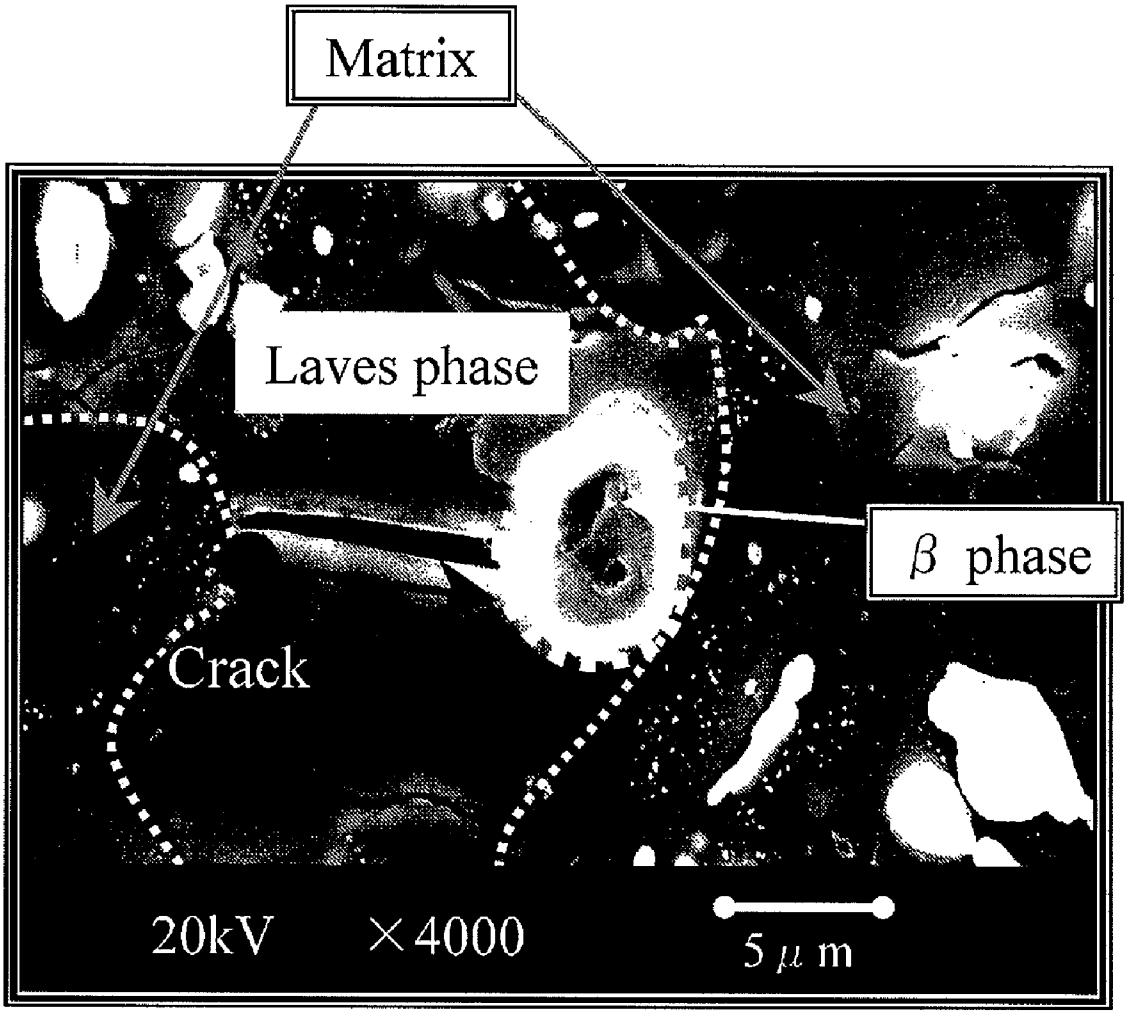

FIGURE 1

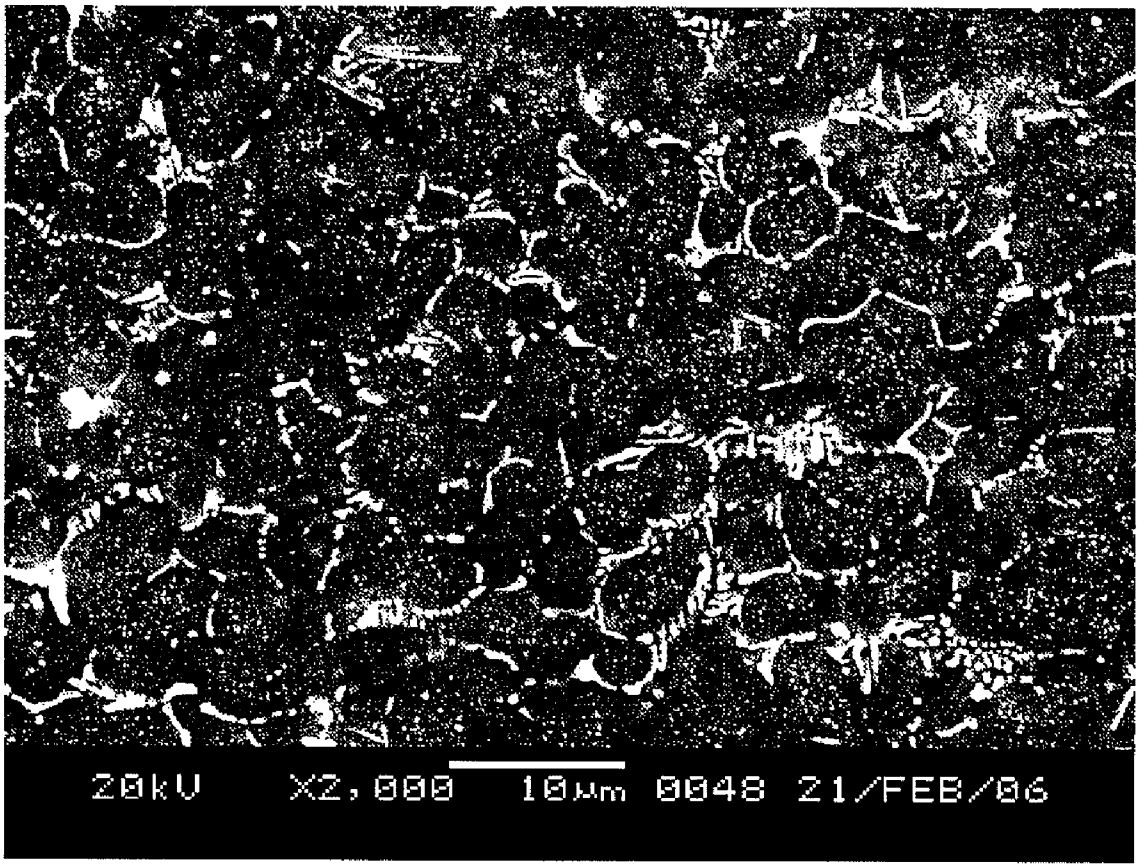

FIGURE 2

HIGH TEMPERATURE SHAPE MEMORY ALLOY, ACTUATOR AND MOTOR

RELATED APPLICATIONS

[0001] This application is a Continuation of PCT Application No. PCT/JP2006/324206, filed Dec. 5, 2006, which claims priority to Japanese Application No. 2006-076560, filed Mar. 20, 2006, the entire contents of both of which are hereby incorporated by reference.

BACKGROUND

[0002] 1. Field of the Inventions

[0003] The present inventions relate to high temperature shape memory alloys which can be used at temperatures in excess of 100° C., as well as actuators and a motors using the shape memory alloys. More particularly, the present inventions relate to high temperature shape memory alloys with peak and reverse martensite transformation temperatures higher than 100° C., as well as actuators and motors using the shape memory alloys.

[0004] 2. Description of the Related Art

[0005] Ti—Ni base alloys are widely known shape memory alloys consisting of Titanium (Ti) and Nickel(Ni) which revert back to their original configuration upon application of heat up to their prescribed operating temperature, remembering their original shape.

[0006] For example, Ti—Ni—Cu alloys are generally known to exhibit shape memory effects at temperature in the range of 200K to 360K Kokai publication Tokukai No. 2002-294371). In addition, Ti—Ni—Nb alloys with martensite start temperatures (M_s) below 50° C. have also been disclosed (Patent publication No. 2539786).

[0007] However, in commercial Ti—Ni alloys including the alloys described in the Kokai publication and patent publication No. 2539786, the peak transformation temperature (M*) is below 70° C. (343K), in the meanwhile, the reverse peak transformation temperature (A*) is below 100° C. (373K). Therefore, the operating temperature of shape memory alloy does not exceed 100° C. Accordingly, conventional Ti—Ni base alloys are difficult for use in high temperature operations as shape memory alloys.

[0008] The below mentioned alloys are generally well known as high temperature shape memory alloys obtained by adding additive elements to Ti—Ni base alloys for operation at high temperature exceeding 100° C.

(1) (Ti—Zr)—Ni Alloys

[0009] In (Ti—Zr)—Ni base alloys, Titanium is substituted by 0-20 mol % (atomic percent) Zirconium (Zr) to obtain a corresponding martensite start temperature (M_s) in the range of 373(K) to 550(K).

(2) (Ti—Hf)—Ni Alloys

[0010] In (Ti—Hf)—Ni base alloys, Titanium is substituted by 0-20 mol % Hafnium (Hf) to obtain a corresponding martensite start temperature (M_s) in the range of 373(K) to 560 (K).

(3) Ti—(Ni—Pd) Alloys

[0011] In Ti—(Ni—Pd) base alloys, Nickel is substituted by 0-50 mol % Palladium (Pd) to obtain a corresponding martensite start temperature (M_s) from 280(K) to 800(K).

(4) Ti—(Ni—Au) Alloys

[0012] In Ti—(Ni—Au) base alloys, Nickel(Ni) is substituted by 0-50 mol % Gold(Au) to obtain a corresponding martensite start temperature (M_s) from 300(K) to 850(K).

(5) Ti—(Ni—Pt) Alloys

[0013] In Ti—(Ni—Pt) base alloys, Nickel is substituted by 0-50 mol % Platinum (Pt) to obtain a corresponding martensite start temperature (M_s) from 280(K) to 1300(K).

(6) Ti—Al Alloys

[0014] In Ni—Al base alloys comprising 30-36 mol % Aluminum (Al) and a balance of Nickel (Ni), a corresponding martensite start temperature (M_s) in the range of 273(K) to 1000(K) is obtained.

(7) Ti—Nb Alloys

[0015] In Ti—Nb alloys comprising 10-28 mol % Niobium (Nb) and a balance of Titanium (Ti), a corresponding martensite start temperature (M_s) in the range of 173(K) to 900(K) is obtained.

(8) Ti—Pd Alloys

[0016] As described in Kokai publication Tokukai No. Hei 11-36024 Ti—Pd base alloys comprising 48 at %-50 at % Palladium (Pd) and 50 at %-52 at % Ti possess a reverse transformation finish temperature (A_f) in excess of 560° C. (833K).

(9) Ti—Ta Alloys

[0017] As described in Ikeda, et al. (Masahiko Ikeda, Shinya Komatsu and Yuichiro Nakamura, Effects of Sn and Zr Additions on Phase Constitution and Aging Behavior Ti-50 mass % Ta Alloys Quenched from β Singe Phase Region, Materials Transactions, The Japan Institute of Metals, page 1106-1112, issue 4, volume 45, 2004), alloys comprising Tantalum 50 mass % (less than 30 mol % if converted to mol percentage) and a balance of Titanium, or Ti—Ta based alloys with 4 mass % Tin (Sn) or 10 mass % Zirconium (Zr) molten into, possess a shape recovery start temperature in excess of 150° C. (423K).

SUMMARY OF THE INVENTIONS

[0018] The conventional high temperature shape memory alloys No. 1 and 2 described above are brittle and thus break easily, which results in poor machinability and lead to failure in cold working.

[0019] In shape memory alloys Nos. 3-5 and 8, in addition to poor machinability, the addition of high priced additive elements (Pd, Au, Pt) make the alloys quite expensive.

[0020] With respect to shape memory alloy No. 6, in addition to poor machinability, precipitation of Ni5Al3 weakens the structural stability of the alloy and embrittles the alloy. Therefore, repeated operation of the alloy at temperatures over 200° C. is impossible. That is to say, the alloy does not exhibit shape memory effects.

[0021] For the above-mentioned shape memory alloy No. 7, even though it possesses good machinability, formation of ω phase, which results in poor structural stability and causes the loss of shape memory property at over 100° C., lowers the

transformation temperature. Therefore the alloy fails for repeated operation. That is to say, the alloy does not exhibit shape memory effects.

[0022] For the above-mentioned shape memory alloy No. 9, it fails for repeated operation due to its relative ease of plastic deformation. Furthermore, easy formation of ω phase during operation results in loss of shape memory property.

[0023] As a result, based on the conventional high temperature shape memory technology described in alloys (1) and (2), the below-described invention were carried out through large amount of experiments and research work in order to improve machinability of Ti—Ni—Zr alloys and Ti—Ni—Hf alloys.

[0024] Accordingly, embodiments of the present disclosure address the problems of the prior art and provide a high temperature shape memory alloys which have good machinability and, in the meanwhile, are suitable for repeated high temperature operation.

EMBODIMENT 1

[0025] A high temperature shape memory alloy is provided in Embodiment 1 to solve these technical problems, where the alloy consists of 34.7 mol %-48.5 mol % Nickel, at least one of Zirconium or Hafnium as transformation temperature increasing additive element, with a total content of 6.8 mol %-22.5 mol %; at least one of Niobium or Tantalum as machinability improving additive element, with a total content of 1 mol %-30 mol %, Boron below 2 mol %, and the balance Titanium; and impurities.

[0026] With respect to high temperature shape memory alloys having the components of Embodiment 1, since the alloys consist of 34.7 mol %-48.5 mol % Nickel at least one of Zirconium or Hafnium as transformation temperature increasing additive element, with a total content of 6.8 mol %-22.5 mol %, at least one of Niobium or Tantalum as machinability improving additive elements, with a total content of 1 mol %-30 mol %, Boron below 2 mol % and the balance Titanium, high transformation temperatures (peak transformation temperature (M*) or peak reverse transformation temperatures (A*)) in excess of 100° C. are obtained, and cold ductility is also improved. Consequently, Embodiment 1 provides a high temperature shape memory alloy for repeated high temperature operation with improved cold working machinability.

[0027] In addition, the description of Boron below 2 mol % also includes the case of 0 mol % Boron, or no addition of Baron.

Form 1 of Embodiment 1

[0028] High temperature shape memory alloys of form 1 in Embodiment 1 consists of 6.8 mol %-22.5 mol % Zirconium as transformation temperature increasing additive elements and 3 mol %-30 mol % Niobium as machinability improving additives.

[0029] In the high temperature shape memory alloys of Form 1 in Embodiment 1, since the alloys consist of 6.8 mol %-22.5 mol % Zirconium and 3 mol %-30 mol % Niobium, high peak reverse transformation temperature (A*) in excess of 100° C. is obtained In the meanwhile, cold working can be performed with high ductility.

Form 2 of Embodiment 1

[0030] High temperature shape memory alloys of form 2 in Embodiment 1 consist of 6.8 mol %-18 mol % Hafnium as transformation temperature increasing additive elements and 3 mol %-20 mol % Niobium as machinability improving additive elements.

[0031] In the high temperature shape memory alloys of Form 2 in Embodiment 1 since the alloys consist of 6.8 mol %-18 mol % Hafnium and 3 mol %-20 mol % Niobium, high peak reverse transformation temperatures (A*) in excess of 100° C. are obtained In the meanwhile, cold working can be performed with improved ductility.

Form 3 of Embodiment 1

[0032] High temperature shape memory alloys of form 3 in Embodiment 1 consists of 6.8 mol %-20 mol % of transformation temperature increasing additive elements and 3 mol %-30 mol % Tantalum as said machinability improving additive elements.

[0033] In the high temperature shape memory alloys of Form 3 in Embodiment 1, since the alloys consist of 6.8 mol %-20 mol % of transformation temperature increasing additive elements and 3 mol %-30 mol % Tantalum as machinability improving additive elements, machinability is improved compared with the case while no Tantalum is added.

Form 4 of Embodiment 1

[0034] The high temperature shape memory alloy of Form 4 in Embodiment 1 with respect to either of the Embodiment 1 or form 3 of Embodiment 1, where the mol ratio of Titanium plus Zirconium and Hafnium to Nickel is in the range of 0.98 to 1.14.

[0035] In the high temperature shape memory alloy of Form 4 in Embodiment 1, since the mol ratio of Titanium plus Zirconium and Hafnium to Nickel is in the range of 0.98 to 1.14, high peak reverse transformation temperature (A*) in excess of 100° C. is obtained. In the meanwhile, cold working can be performed with high ductility.

EMBODIMENT 2

[0036] An actuator is provided in Embodiment 2 to solve the above-mentioned technical problems, where the actuator is made of the high temperature shape memory alloys described in either the Embodiment 1 or forms 1 through 4 of Embodiment 1.

[0037] In the actuator in Embodiment 2, since the actuator is made of the high temperature shape memory alloy of either the Embodiment 1 or forms 1 through 4 of Embodiment 1, it is capable to perform cold working. In addition, high temperature applications are possible with the help of its high transformation temperatures and shape memory effects.

EMBODIMENT 3

[0038] A motor is provided in Embodiment 3 to solve the above-mentioned technical problems, where the motor pos-

sesses a flux adjustment valve made of the high temperature shape memory alloys described in either Embodiment 1 or forms 1 through 4 of Embodiment 1.

[0039] In the motor in Embodiment 3, since the motor possesses a flux adjustment valve made of the high temperature shape memory alloys described in either Embodiment 1 or forms 1 through 4 of Embodiment 1, high temperature operations can be performed with high transformation temperatures and shape memory effects.

[0040] The present embodiments provide shape memory alloys capable of repeated high temperature operation with high machinability.

BRIEF DESCRIPTION OF THE DRAWINGS

[0041] FIG. **1** shows a scanning electron microscope image of alloy No. 7 in an embodiment of the present disclosure.

[0042] FIG. **2** shows a scanning electron microscope image of alloy No. 8 in an embodiment of the present disclosure.

DETAILED DESCRIPTION

[0043] Embodiments of the present disclosure are described in detail below.

[0044] As embodiments and comparative examples of the present disclosure, 55 alloy specimens, Nos. 1 to 55, were provided as shown in Tables 1 to 10 and corresponding experiments were carried out. Specimens were prepared by the below described process including steps (1) to (3).

[0045] In step 1, each metallic element is measured by mol %, and then molten by means of arc melting method to make alloy ingots. Namely, alloy No. 2 ($Ti—Ni_{49.5}—Zr_{10}$) has a composition expressed as 49.5 mol % Ni, 10 mol % Zr and the balance Ti (40.5 mol %).

[0046] In step 2, the resultant alloy ingots are subjected to homogenization heat treatment for 2 hours (7.2 ks) at 950° C.

[0047] In step 3, billets (test pieces) 15 mm long, 10 mm wide, and 1 mm thick are cut off by electric discharge machining.

Machinability Evaluation Tests

[0048] Machinability evaluation tests were carried out to evaluate the machinability of the alloys manufactured by the above mentioned methods. Machinability evaluation tests were carried out through cold rolling at deformations up to 60%. The break rolling ratio of test pieces, with test pieces breaking down at deformations up to 60%, was measured to evaluate machinability.

Transformation Temperature Measurement Tests

[0049] In this test, cold rolled test pieces were heat-treated for 1 hour at 700° C. to measure the martensite peak transformation temperature (M*) and peak reverse transformation temperature (A*) of each alloy by means of Differential Scanning Calorimetry (DSC).

[0050] As comparative examples, the composition of ternary Ti—Ni—Zr alloys Nos. 1 to 4, along with the mol ratio of Ti plus Zr to Ni, break rolling ratio (%), martensite peak transformation temperature (M*, ° C.) and peak reverse transformation temperature (A*, ° C.) are provided in Table 1.

TABLE 1

Machinability of Ti—Ni—Zr alloys and transformation temperatures

	No.	composition	Component(mol %) Ti	Ni	Zr	Nb	(Ti + Zr)/ Ni	Break rolling ratio (%)	transformation temperature M*	A*
Comparative example	1	$Ti—Ni_{49.5}—Zr_7$	balance	49.5	7	—	1.02	42	81	132
	2	$Ti—Ni_{49.5}—Zr_{10}$	balance	49.5	10	—	1.02	30	102	155
	3	$Ti—Ni_{49.5}—Zr_{15}$	balance	49.5	15	—	1.02	10	179	219
	4	$Ti—Ni_{49.5}—Zr_{20}$	balance	49.5	20	—	1.02	9	270	325

[0051] As embodiments of the present disclosure, the composition of quaternary Ti—Ni—Zr—Nb alloys Nos. 5 to 7, along with the mol ratio of Ti plus Zr to Ni, break rolling ratio (%), martensite peak transformation temperature (M*, ° C.), and peak reverse transformation temperature (A*, ° C.) are shown respectively in Table 2.

[0052] Furthermore, alloys No. 5-7 are derived by fixing Ti and Zr content (mol %) of alloy No. 3, and then substituting Ni content by Nb.

TABLE 2

Machinability of Ti—Ni—Zr—Nb alloys and transformation temperature

	No.	composition	Component(mol %) Ti	Ni	Zr	Nb	(Ti + Zr)/ Ni	Break rolling ratio (%)	transformation temperature M*	A*
Embodiment	5	$Ti—Ni_{48.5}—Zr_{15}—Nb_1$	balance	48.5	15	1	1.04	17	149	190
	6	$Ti—Ni_{46.5}—Zr_{15}—Nb_3$	balance	46.5	15	3	1.09	50	140	184
	7	$Ti—Ni_{44.5}—Zr_{15}—Nb_5$	balance	44.5	15	5	1.14	46	131	171

[0053] As embodiments and comparative examples of the present invention, the composition of quaternary Ti—Ni—Zr—Nb alloys Nos. 8 to 12, along with the mol ratio of Ti plus Zr to Ni, break rolling ratio (%), martensite peak transformation temperature (M*, ° C.), and peak reverse transformation temperature (A*, ° C.) are shown respectively in Table 3.

[0054] Furthermore, alloys No. 8-12 are derived by fixing the mol ratio of Ti, Ni and Zr to 35.5 mol %, 49.5%, and 15 mol % respectively, and then substituting Ti, Ni, and Zr as a whole by Nb.

TABLE 3

Machinability of Ti—Ni—Zr—Nb alloys and transformation temperatures

	No.	Composition	Component(mol %) Ti	Ni	Zr	Nb	(Ti + Zr)/ Ni	Break rolling ratio (%)	transformation temperature M*	A*
Embodiment	8	$(Ti—Ni_{49.5}—Zr_{15})_{95}—Nb_5$	balance	47.0	14.3	5	1.02	35	134	180
	9	$(Ti—Ni_{49.5}—Zr_{15})_{90}—Nb_{10}$	balance	44.6	13.5	10	1.02	Over 60	110	162
	10	$(Ti—Ni_{49.5}—Zr_{15})_{80}—Nb_{20}$	balance	39.6	12.0	20	1.02	Over 60	90	139
	11	$(Ti—Ni_{49.5}—Zr_{15})_{70}—Nb_{30}$	balance	34.7	10.5	30	1.02	Over 60	72	122
Comparative example	12	$(Ti—Ni_{49.5}—Zr_{15})_{99}—Nb_1$	balance	49.0	14.9	1	1.02	10	157	198

[0055] As embodiments and comparative examples of the present disclosure, the composition of quaternary Ti—Ni—Zr—Nb alloys Nos. 13 to 17, along with the mol ratio of Ti plus Zr to Ni, break rolling ratio (%), martensite peak transformation temperature (M*, ° C.), and peak reverse transformation temperature (A*, ° C.) are shown respectively in Table 4.

[0056] Additionally, with regard to the alloys No. 16 and 17, since the transformation temperature is not identified in the experiment, it can be concluded that transformation temperature is too low to be observed.

TABLE 4

Machinability of Ti—Ni—Zr—Nb alloys and transformation temperatures

	No.	Composition	Component(mol %) Ti	Ni	Zr	Nb	(Ti + Zr)/ Ni	Break rolling ratio (%)	transformation temperature M*	A*
Embodiment	13	$(Ti—Ni_{50.5}—Zr_{15})_{90}—Nb_{10}$	balance	45.5	13.5	10	0.98	Over 60	74	121
	14	$(Ti—Ni_{48.5}—Zr_{15})_{95}—Nb_5$	balance	46.1	14.3	5	1.06	23	132	177
	15	$(Ti—Ni_{50.5}—Zr_{15})_{95}—Nb_5$	balance	48	14.3	5	0.98	30	104	145
Comparative	16	$(Ti—Ni_{55.0}—Zr_{15})_{90}—Nb_{10}$	balance	49.5	13.5	10	0.82	5	—	—
	17	$(Ti—Ni_{35.0}—Zr_{15})_{90}—Nb_{10}$	balance	31.5	13.5	10	1.86	8	—	—

[0057] As embodiments and comparative examples of the present disclosure, the composition of quaternary Ti—Ni—Zr—Nb alloys Nos. 18 to 26, as well as the mol ratio of Ti plus Zr to Ni, break rolling ratio (%), martensite peak transformation temperature (M*, ° C.), and peak reverse transformation temperature (A*, ° C.) are shown respectively in Table 5.

TABLE 5

Machinability of Ti—Ni—Zr—Nb alloys and transformation temperatures

	No.	Composition	Content(mol %) Ti	Ni	Zr	Nb	(Ti + Zr)/ Ni	Break rolling ratio (%)	transformation temperature M*	A*
Embodiment	18	$(Ti—Ni_{49.5}—Zr_{10})_{95}—Nb_5$	balance	47.0	9.5	5	1.02	Over 60	52	124
	19	$(Ti—Ni_{49.5}—Zr_{10})_{90}—Nb_{10}$	balance	44.6	9.0	10	1.02	Over 60	41	109
	20	$(Ti—Ni_{49.5}—Zr_{20})_{90}—Nb_{10}$	balance	44.6	18.0	10	1.02	38	182	236
	21	$(Ti—Ni_{49.5}—Zr_{25})_{90}—Nb_{10}$	balance	44.6	22.5	10	1.02	28	325	408
	22	$(Ti—Ni_{49.5}—Zr_{25})_{70}—Nb_{30}$	balance	34.7	17.5	30	1.02	Over 60	450	580
	23	$(Ti—Ni_{49.5}—Zr_7)_{97}—Nb_3$	balance	48.0	6.8	3	1.02	Over 60	41	102

TABLE 5-continued

Machinability of Ti—Ni—Zr—Nb alloys and transformation temperatures

	No.	Composition	Content(mol %) Ti	Ni	Zr	Nb	(Ti + Zr)/ Ni	Break rolling ratio (%)	transformation temperature M*	A*
Comparative example	24	$(Ti—Ni_{49.5}—Zr_{30})_{90}—Nb_{10}$	balance	44.6	27.0	10	1.02	5	—	—
	25	$(Ti—Ni_{49.5}—Zr_{20})_{50}—Nb_{50}$	balance	24.8	10.0	50	1.02	Over 60	—	—
	26	$(Ti—Ni_{49.5}—Zr_{5})_{90}—Nb_{10}$	balance	44.6	4.5	10	1.02	Over 60	5	75

[0058] As embodiments and comparative examples of the present invention, the composition of quaternary Ti—Ni—Hf—Nb alloys and quinary Ti—Ni—Zr—Hf—Nb Nos. 27 to 37, along with the mol ratio of Ti plus Zr and Hf to Ni, break rolling ratio (%), martensite peak transformation temperature (M*, ° C.) and peak reverse transformation temperature (A*, ° C.), are given respectively in Table 6.

[0059] Furthermore, alloys No. 28 and 29 correspond to alloys 9 and 10, respectively, in which Zr is substituted by Hf and alloy No. 30 corresponds to alloy 20 in which Zr, is substituted by Hf. Besides, alloy No. 31 corresponds to alloy No. 7 in which Zr is substituted by Hf, and alloy No. 32 corresponds to alloy No. 19, in which half of Zr content (10 mol %) is substituted by Hf. In other words, the total content of Zr and Hf (transformation temperature increasing additive elements) is 9 mol % in alloy No. 32 and 12 mol % in alloy No. 33 respectively.

TABLE 6

Machinability of Ti—Ni—Zr—Nb alloys and transformation temperatures

	No.	composition	Content(mol %) Ti	Ni	Zr	Hf	Nb	(Ti + Zr + Hf)/Ni	Break rolling ratio (%)	transformation temperature M*	A*
Embodiment	27	$(Ti—Ni_{49.5}—Hf_{7})_{97}—Nb_{3}$	balance	48.0		6.8	3	1.02	Over 60	75	125
	28	$(Ti—Ni_{49.5}—Hf_{15})_{90}—Nb_{10}$	balance	44.6	—	13.5	10	1.02	Over 60	152	206
	29	$(Ti—Ni_{49.5}—Hf_{15})_{80}—Nb_{20}$	balance	39.6	—	12	20	1.02	Over 60	95	158
	30	$(Ti—Ni_{49.5}—Hf_{20})_{90}—Nb_{10}$	balance	44.6		18	10	1.02	33	193	255
	31	$Ti—Ni_{44.5}—Hf_{15}—Nb_{5}$	balance	44.5	—	15	5	1.14	48	136	185
	32	$(Ti—Ni_{49.5}—Zr_{5}—Hf_{5})_{90}—Nb_{10}$	balance	44.6	4.5	4.5	10	1.02	Over 60	52	121
	33	$(Ti—Ni_{49.5}—Zr_{7.5}—Hf_{7.5})_{80}—Nb_{20}$	balance	39.6	6	6	20	1.02	Over 60	77	141
Comparative example	34	$Ti—Ni_{49.5}—Hf_{7}$	balance	49.5	—	7	—	1.02	40	94	153
	35	$Ti—Ni_{49.5}—Hf_{15}$	balance	49.5	—	15	—	1.02	15	183	228
	36	$Ti—Ni_{49.5}—Hf_{20}$	balance	49.5	—	20	—	1.02	10	265	307
	37	$Ti—Ni_{49.5}—Zr_{7.5}—Hf_{7.5}$	balance	49.5	7.5	7.5	—	1.02	12	179	223

[0060] As embodiments the present disclosure, the composition of quaternary Ti—Ni—Zr—Ta alloys Nos. 38 to 42, along with the mol ratio of Ti plus Zr to Ni, break rolling ratio (%), martensite peak transformation temperature (M*, ° C.), and peak reverse transformation temperature (A*, ° C.) are shown respectively in Table 7.

[0061] Furthermore, alloys 38-42 are derived by fixing the mol ratio of Ti, Ni and Zr to 40.5 mol %, 49.5% and 10 mol % respectively, and then substituting Ti, Ni, and Zr as a whole by Ta.

TABLE 7

Machinability of Ti—Ni—Zr—Ta alloys and transformation temperatures

	No.	composition	Component(mol %) Ti	Ni	Zr	Nb	Ta	(Ti + Zr)/ Ni	Break rolling ratio (%)	transformation temperature M*	A*
Embodiment	38	$(Ti—Ni_{49.5}—Zr_{10})_{95}—Ta_{5}$	balance	47.0	9.5	—	5	1.02	40	97	155
	39	$(Ti—Ni_{49.5}—Zr_{10})_{90}—Ta_{10}$	balance	44.6	9	—	10	1.02	Over 60	98	156
	40	$(Ti—Ni_{49.5}—Zr_{10})_{85}—Nb_{15}$	balance	42.1	8.5	—	15	1.02	Over 60	98	161
	41	$(Ti—Ni_{49.5}—Zn_{10})_{80}—Ta_{20}$	balance	39.6	8	—	20	1.02	Over 60	111	171
	42	$(Ti—Ni_{49.5}—Zr_{10})_{70}—Ta_{30}$	balance	34.7	7	—	30	1.02	Over 60	117	175

[0062] As embodiments of the present disclosure, the composition of quaternary Ti—Ni—Zr—Ta alloys and quinary Ti—Ni—Zr—Nb—Ta, Nos. 43 to 48, along with the mol ratio of Ti plus Zr to Ni, break rolling ratio (%), martensite peak transformation temperature (M*, ° C.), and peak reverse transformation temperature (A*, ° C.) are shown respectively in Table 8.

[0063] Furthermore, the total content of Nb and Ta (machinability improving additive elements) is 10 mol % in alloy No. 48.

[0064] As embodiments and comparative examples of the present disclosure, the composition of quinary Ti—Ni—Zr—Nb—B alloys Nos. 49 to 52, along with the mol ratio of Ti plus Zr to Ni, break rolling ratio (%), martensite peak transformation temperature (M*, ° C.), and peak reverse transformation temperature (A*, ° C.) are shown respectively in Table 9.

[0065] Furthermore, alloys No. 49 to 52 are derived by adding element B (Boron) into Ti—Ni—Zr—Nb based alloys.

TABLE 8

Machinability of Ti—Ni—Zr—Ta—(Nb) alloys and transformation temperatures

	No.	composition	Content(mol %) Ti	Ni	Zr	Nb	Ta	(Ti + Zr)/ Ni	Break rolling ratio (%)	transformation temperature M*	A*
Embodiment	43	$(Ti—Ni_{49.5}—Zr_{15})_{95}—Ta_5$	balance	47.0	14.3	—	5	1.02	15	180	229
	44	$(Ti—Ni_{49.5}—Zr_{15})_{90}—Ta_{10}$	balance	44.6	13.5	—	10	1.02	23	165	219
	45	$(Ti—Ni_{49.5}—Zr_{15})_{85}—Ta_{15}$	balance	42.1	12.8	—	15	1.02	30	169	224
	46	$(Ti—Ni_{49.5}—Zr_{15})_{80}—Ta_{20}$	balance	39.6	12.0	—	20	1.02	Over 60	179	231
	47	$(Ti—Ni_{49.5}—Zr_{25})_{80}—Ta_{20}$	balance	39.6	20.0	—	20	1.02	45	327	412
	48	$(Ti—Ni_{49.5}—Zr_{15})_{90}—Nb_5—Ta_5$	balance	44.6	13.5	5	5	1.02	40	142	203

TABLE 9

Machinability of Ti—Ni—Zr—Nb—B alloys and transformation temperatures

	No.	composition	Content(mol %) Ti	Ni	Zr	Nb	B	(Ti + Zr)/ Ni	Break rolling ratio (%)	transformation temperature M*	A*
Embodiment	49	$(Ti—Ni_{49.5}—Zr_{15})_{94.8}—Nb_5—B_{0.2}$	balance	46.9	14.2	5	0.2	1.02	40	140	185
	50	$(Ti—Ni_{49.5}—Zr_{15})_{93}—Nb_5—B_2$	balance	46.0	14.0	5	2	1.02	36	144	191
	51	$(Ti—Ni_{49.5}—Zr_{20})_{89.5}—Nb_{10}—B_{0.5}$	balance	44.3	17.9	10	0.5	1.02	40	217	271
Comparative example	52	$(Ti—Ni_{49.5}—Zr_{15})_{92}—Nb_5—B_3$	balance	45.5	13.8	5	3	1.02	20	135	179

[0066] As embodiments of the present invention, the composition of Ti—Ni—Zr—Hf—Nb—Ta—B based multi-component alloys No. 53 to 55, along with the mol ratio of Ti plus Zr and Hf to Ni, break rolling ratio (%), martensite peak transformation temperature (M*, ° C.), and peak reverse transformation temperature (A*, ° C.), are shown in Table 10.

TABLE 10

Machinability of Ti—Ni—Zr—Hf—Nb—Ta—B alloys and transformation temperatures

	No.	composition	Content(mol %) Ti	Ni	Zr	Hf	Nb	Ta	B	(Ti + Zr + Hf)/Ni	Break rolling ratio (%)	transformation temperature M*	A*
Embodiment	53	$(Ti—Ni_{49.5}—Hf_{15})_{85}—Nb_5—Ta_{10}$	Balance	42.1	—	12.8	5	10	—	1.02	Over 60	125	178
	54	$(Ti—Ni_{49.5}—Zr_{7.5}—Hf_{7.5})_{90}—Nb_5—Ta_5$	Balance	44.6	6.8	6.8	5	5	—	1.02	45	112	168
	55	$(Ti—Ni_{49.5}—Zr_{7.5}—Hf_{7.5})_{91.5}—Nb_5—Ta_3—B_{0.5}$	Balance	45.3	6.9	6.9	5	3	0.5	1.02	42	118	171

[0067] FIG. **1** shows a scanning electron microscope image of alloy No. 7 in an embodiment of the present disclosure.

[0068] The following conclusion can be drawn from the forgoing description of the experiment results. The relatively low rolling ratio of Ti—Ni—Zr based ternary alloys No. 1 to 4 in the comparative examples indicates poor machinability. Besides, while the transformation temperature (M* and A*) increases with increasing Zr (Zr, transformation temperature increasing additive) content, the rolling ratio decreases, resulting in reduced machinability.

[0069] In comparison to the forgoing result, as shown in Table 2, in the case of the quaternary Ti—Ni—Zr—Nb base alloys Nos. 5 to 7 derived from substitution of Ni in alloy No. 3 of the comparative example by Nb (machinability improvement additive element), rolling ratio increases thus machinability improves accordingly. In addition, transformation temperature (M* and A*) in excess of 100° C. makes it possible for high temperature operation 100° C. Particularly, even though the transformation temperature tends to decrease with increasing Nb content, it exhibits a small change in amplitude indicating no drastic drop of transformation temperature occurred.

[0070] As a result, with improved machinability, alloys No. 5 to 7 are suitable for high temperature operation as high temperature shape memory alloys. Furthermore, even with improved break rolling ratio, existence of a large amount of fine cracks are observed in alloys No. 5 to 7. As shown in FIG. **1** of the SEM image by Scanning Electric Microscope, together with the hard brittle Laves phase that forms in alloy No. 7 after rolling, the soft β phase liable to plastic deformation precipitates, which hinders the development of cracks, appeared on the interfaces of said Laves phase. As a result, machinability is improved.

[0071] FIG. **2** shows a scanning electron microscope image of alloy No. 8 in embodiment of the present disclosure.

[0072] In Table 3, in the case of quaternary Ti—Ni—Zr—Nb alloys Nos. 8 to 12, embodiments of which are derived by fixing the mol ratio of $Ti—Ni_{49.5}—Zr_{15}$ and then substituting Ti, Ni, and Zr as a whole by Nb, high peak reverse transformation temperature (A*) exceeding 100° C. and relatively high martensite transformation temperature (A*) are obtained. Moreover, even though no significant improvement in ductility was observed with 1 mol % Nb added (alloy No. 11 of comparative example), ductility increases when Nb content is greater than 3 mol %. In particular, when Nb content exceeds 10 mol %, rolling ratio reached 60% for alloys No. 9 to 11. Furthermore, with respect to alloys No. 8 to 11, compared to alloys No. 5 to 7, machinability was improved while no significant fine crack developed. In the SEM image of FIG. **2**, soft β phase precipitated on crystal interfaces, as well as within the crystal grains, for alloy No. 8 after rolling. Consequently machinability is improved.

[0073] In Tables 1 to 4, in the case of alloys Nos. 13 to 15 and alloy No. 7, when the mol ratio of metallic components to Nickel is about 1, compared with alloys No. 3 and 12 while Zr content is 15 mol %, ductility increases. However, when the mol ratio of metallic components to Nickel is 0.82, which deviates substantially from the value 1 for alloy No. 16, or 1.86 as for alloy No. 17, ductility decreases and machinability is reduced. At the same time it is identified a drastic drop in transformation temperature (M* and A*)

[0074] In Table 5, with respect to alloys No. 18 to 23, even though the content of Zr which is added to increase the transformation temperature (M* and A*) reaches the degree that may reduce machinability, through addition of Nb by 3 to 30 mol %, machinability is able to be improved without reducing transformation temperature. Particularly in the case of alloy No. 22, an extremely high transformation temperature, exceeding 400° C., is obtained with 60% of extremely high machinability. In alloy No. 24, when the content of added Zr reaches 27%, the test piece broke at merely 5% deformation, even with 10 mol % Nb added. As shown with alloy No. 25, rolling ratio is in excess of 60% when 50 mol % Nb was added, which indicates extraordinarily high machinability; however, transformation temperature was not identified. On the other hand, when 4.5 mol % Zr was added in the case of alloy No. 26, high machinability of over 60% in rolling ratio was obtained with 10 mol % addition of Nb, transformation temperature was lowered to below 100° C.

[0075] As shown in Table 6 with respect to alloys No. 27 to 37, in the case of Ti—Ni—Hf based alloys, which possess approximately the same properties as Ti—Ni—Zr based alloys and are also poor in machinability, high temperature shape memory alloys having high transformation temperature with improved machinability are obtained through addition of Nb. Particularly, in the case of alloy No. 27, compared with alloys Nos. 1, 23 and 34, equal or better physical properties (transformation temperature and rolling ratio) are obtained even when Zr is substituted by Hf (transformation temperature increasing additive), same as the case of Zr. Similarly, it can also be seen that equal or better properties (transformation temperature and rolling ratio) are obtained when Zr was substituted by Hf (transformation temperature increasing additive) as we compare alloy No. 28 compare with alloys Nos. 3, 9 and 35, alloy No. 29 with alloys No. 10, alloy No. 30 with alloys Nos. 20 and 36, alloy No. 31 with alloy 7, alloy 32 with alloys Nos. 2 and 19, alloy No. 33 with alloys Nos. 10, 29 and 37, which indicates that by adding Nb the same improvement effect is achieved.

[0076] As a result, it is understood that by adding Nb to Ti—Ni—Zr (or Hf) based alloys, high temperature shape memory alloys with high machinability and high transformation temperature are obtained.

[0077] As shown in Tables 7 and 8 with respect to alloys Nos. 38 to 48, by adding Ta (machinability improving additive) or the combination of Ta and Nb instead of Nb, to Ti—Ni—Zr based alloys, high temperature shape memory alloys of high machinability with high transformation temperature are obtained. In addition, it shows that with increasing Ta content, rolling ratio increases and transformation temperature increases as well.

[0078] In particular, comparing alloys Nos. 38 and 39 with alloys Nos. 18 and 19 in which Nb is added, it can be seen that alloys Nos. 38 and 39 possess higher transformation temperature; besides, as we compare alloys Nos. 43, 44 and 46 with alloys Nos. 8, 9, 10 and 3, even though adding Ta to alloys No. 43, 44, and 46 exhibits little effect to improve rolling ratio compared with adding Nb to alloys Nos. 8 to 10, better rolling ratio and higher transformation temperature were obtained compared respectively with alloy No. 3 and alloys Nos. 8 to 10 with added Nb.

[0079] Furthermore, as alloy No. 48 was compared with alloys Nos. 44, 9, and 3, in the case of alloy 48 with combined addition of Ta and Nb, the rolling ratio is improved compared with alloy No. 44 with only Ta added, and yet the transformation temperature is increased compared with alloy No. 9 while only Nb is added.

[0080] As shown in Table 9, with respect to alloys Nos. 49 to 52, by adding Nb and further adding B (Boron, temperature increasing and machinability improving additive element), rolling ratio is improved with increased transformation temperature compared with alloys Nos. 8 and 20 while no B is added. In addition, comparing alloys Nos. 49, 50, and 52 with alloy No. 8, it can be seen that the improving effect tends to be

weakened with increasing B content, indicating a small amount of B addition is preferable.

[0081] As shown in Table 10 with respect to alloys Nos. 53 to 55, by adding Nb, Ta and B to Ti—Ni—Hf or Ti—Ni—Zr—Hf alloys, a transformation temperature exceeding 100° C. is obtained and rolling ratio is also improved compared with alloys No. 35 and 37.

[0082] In the above description, the preferred exemplary embodiments of the present invention were set forth, it will be understood that the invention is not limited to the specific forms shown, modification may be made without departing from the scope of the present invention as expressed in the claims.

INDUSTRIAL APPLICATIONS

[0083] Since the afore-described shape memory alloys do not lose their shape memory effect during repeated use at high temperature, they can be used as valves inside gas channels of motors (engines of automobiles, aircrafts, or gas turbine) for high temperature operation, when heated, channel area is regulated with the help of the shape memory effect; when cooled, channel area is reversed back by a spring used for deforming the valve. Besides, they can also be used as lubricant supplying valves of high speed rotating shafts. In addition, these alloys can be used as safety devices for power supply of household electric appliance at high temperature operation. Furthermore, they can also be used as actuators for high temperature operation. In the case of actuators, they also exhibit improved responsiveness resulting from increased cooling speed.

What is claimed is:

1. A high temperature shape memory alloy, wherein said alloy consists of 34.7 mol %-48.5 mol % Ni, at least either Zirconium or Hafnium as transformation temperature increasing additive elements, with the sum of which 6.8 mol % to 22.5 mol %; at least either Niobium or Tantalum as machinability improving additives, with the sum of which 1 mol % to 30 mol %; and Boron less than 2 mol %; and Titanium and impurities as the balance.

2. A high temperature shape memory alloy according to claim **1**, wherein said alloy consists of 6.8 mol % to 22.5 mol % Zirconium as said transformation temperature increasing additives; and 3 mol % to 30 mol % Niobium as said machinability improving additives.

3. A high temperature shape memory alloy according to claim **1**, wherein said alloy consists of 6.8 mol % to 18 mol % Hafnium as said transformation temperature increasing additives; and 3 mol % to 20 mol % Niobium as said machinability improving additives.

4. A high temperature shape memory alloy according to claim **1**, wherein said alloy consists of 6.8 mol % to 20 mol % said transformation temperature increasing additives; and 3 mol % to 30 mol % Tantalum as said machinability improving additives.

5. A high temperature shape memory alloy according to claim **1**, wherein the mol ratio of Titanium plus Zirconium and Hafnium to Nickel is in the range of 0.98 to 1.14.

6. An actuator, wherein the said actuator is made of the high temperature shape memory alloy described in claim **1**.

7. A motor equipped with a flux adjusting valve, wherein the said flux adjusting valve is made of the high temperature shape memory alloy described in claim **1**.

8. A shape memory alloy, comprising:
- nickel (Ni);
- at least one of zirconium (Zr) and hafnium (Hf) as transformation temperature increasing additive elements;
- at least one of niobium (Nb) and tantalum (Ta) as machinability improving additives; and
- boron (B) in a concentration ranging between 0 mol %-2 mol %;
- wherein the mol ratio of Titanium plus Zirconium and Hafnium to Nickel is between 0.98 to 1.14.

9. The alloy of claim **8**, wherein nickel is present in a concentration ranging between 34.7 mol %-48.5 mol %.

10. The alloy of claim **8**, wherein the sum of the concentration of zirconium and hafnium ranges between 6.8 mol %-22.5 mol %.

11. The alloy of claim **8**, wherein the sum of the concentration of niobium and tantalum ranges between 1 mol %-30 mol %.

12. The alloy of claim **8**, wherein the concentration of zirconium ranges between 6.8 mol %-22.5 mol % and the concentration of niobium ranges between 3 mol %-30 mol %.

13. The alloy of claim **8**, wherein the concentration of hafnium ranges between 6.8 mol %-18 mol % and the concentration of niobium ranges between 3 mol %-20 mol %.

14. The alloy of claim **8**, wherein the sum of the concentration of zirconium and hafnium ranges between 6.8 mol %-20 mol % and the concentration of tantalum ranges between 3 mol %-30 mol %.

15. The alloy of claim **8**, wherein the peak reverse transformation temperature (A*) is greater than 100° C.

16. A method of making a shape memory alloy part, comprising:
- providing a shape memory alloy composition comprising:
  - nickel in a concentration ranging between 34.7 mol %-48.5 mol %;
  - at least one of zirconium and hafnium, wherein the total concentration zirconium plus hafnium ranges between 1 mol %-30 mol %;
  - at least one of niobium and tantalum, wherein the total concentration niobium plus tantalum ranges between 6.8 mol %-22.5 mol %; and
  - boron (B) in a concentration below 2 mol %;
  - wherein the concentration of the elements is selected such that the mol ratio of Titanium plus Zirconium and Hafnium to Nickel is between 0.98 to 1.14; and
- forming the shape memory alloy composition into the part.

17. The method of claim **16**, wherein the concentration of zirconium ranges between 6.8 mol %-22.5 mol % and the concentration of niobium ranges between 3 mol %-30 mol %.

18. The method of claim **16**, wherein the concentration of hafnium ranges between 6.8 mol %-18 mol % and the concentration of niobium ranges between 3 mol %-20 mol %.

19. The method of claim **16**, wherein the sum of the concentration of zirconium and hafnium ranges between 6.8 mol %-20 mol % and the concentration of tantalum ranges between 3 mol %-30 mol %.

20. The method of claim **16**, wherein the part comprises at least one of an actuator and a flux adjusting value configured for use with a motor.

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