



US 20080031769A1

(19) **United States**(12) **Patent Application Publication**
Yeh(10) **Pub. No.: US 2008/0031769 A1**(43) **Pub. Date: Feb. 7, 2008**(54) **HIGH-TEMPERATURE RESISTANT ALLOY
WITH LOW CONTENTS OF COBALT AND
NICKEL**(76) Inventor: **Jien-Wei Yeh, Hsinchu (TW)**

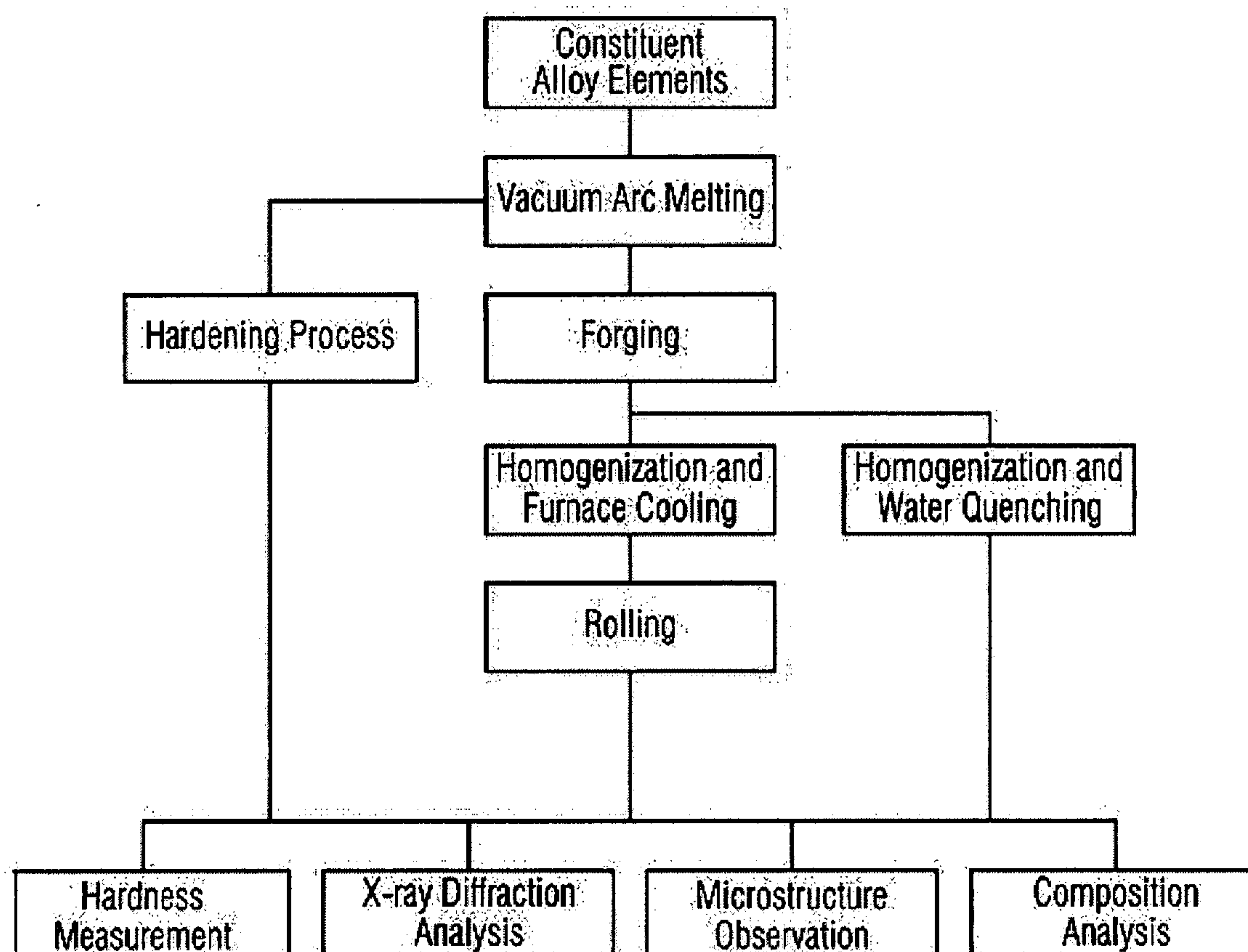
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SUNNYVALE, CA 94085**(21) Appl. No.: **11/724,976**(22) Filed: **Mar. 16, 2007**(30) **Foreign Application Priority Data**

Jul. 28, 2006 (TW) 95127668

Publication Classification(51) **Int. Cl.**
C22C 30/00 (2006.01)(52) **U.S. Cl. 420/580**(57) **ABSTRACT**

High-temperature resistant alloys, with low Co and Ni contents and a predominant face-centered cubic (FCC) matrix, are formed by selecting an appropriate combination of elements based on a 'multi-principle-element alloy design'. It exhibits excellent properties in terms of workability, toughness, high-temperature strength, corrosion resistance and oxidation resistance. These alloys are designed to incorporate five to seven principal elements, which include Co, Cr, Fe, and Ni, plus one, or a combination of Al, Mo, and Ti. The Co and Ni elements have contents of 20 to 35 atomic percent, and those of Cr and Fe are between 12.5 and 20 atomic percent. The sum of the Co, Ni, Cr, and Fe is not less than 65 atomic percent, and the sum of Al, Mo, and Ti contents is between 5 and 25 atomic percent. The properties of the alloys can be further modified by the addition of minor elements, such as Ag, B, C, Cu, Mn, Nb, Ta, Si, V, W, Y, and Zr, whose sum does not exceed 10 atomic percent.



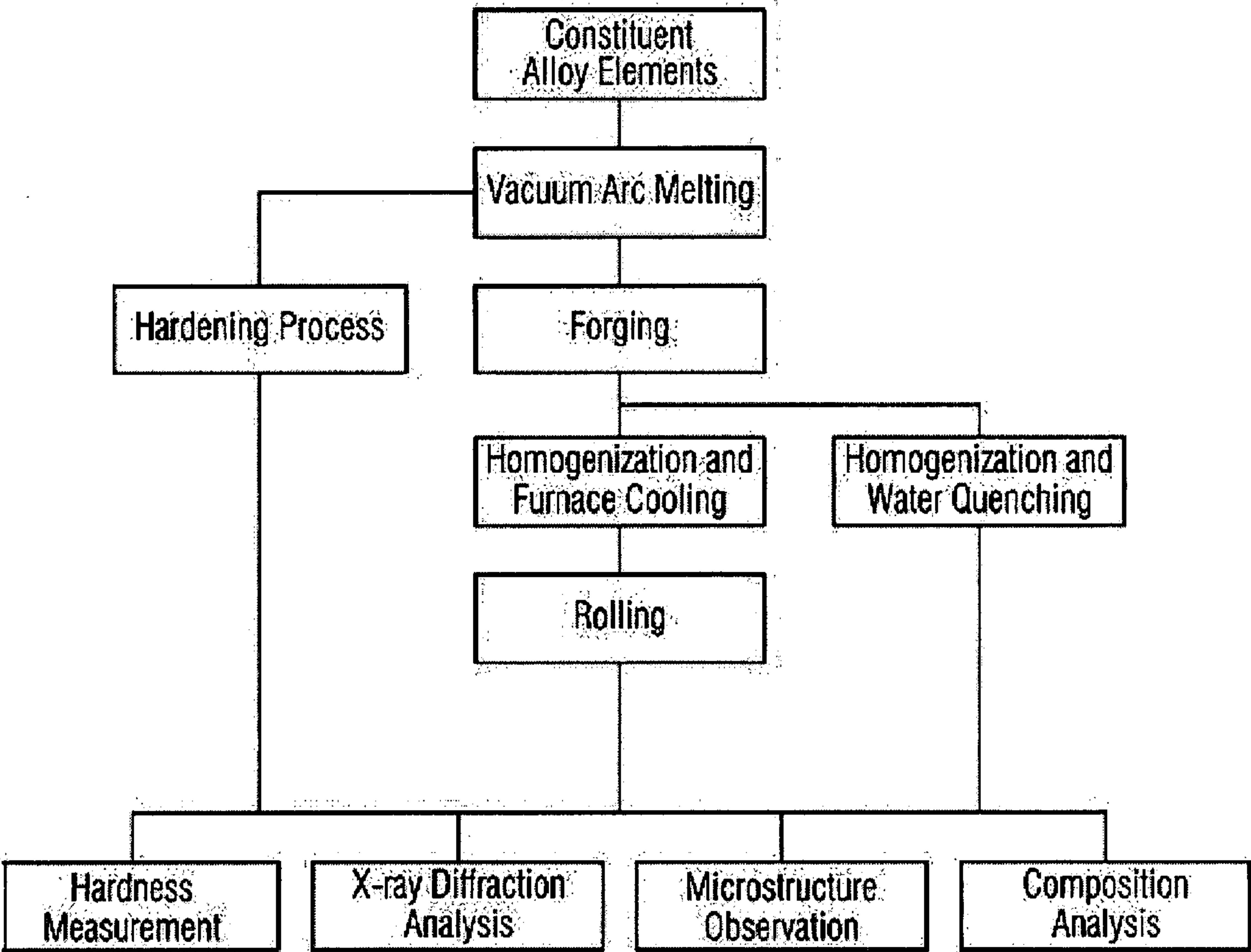


FIG. 1

HIGH-TEMPERATURE RESISTANT ALLOY WITH LOW CONTENTS OF COBALT AND NICKEL

BACKGROUND OF THE INVENTION

[0001] a) Field of the Invention

[0002] The invention is a novel high-temperature resistant alloy that requires only low contents of cobalt and nickel, and, importantly, possesses a predominantly face-centered cubic crystal structure (FCC). The alloy is based on a novel concept of multi-principal-element design.

[0003] b) Description of Related Art

[0004] Alloy compositions, to date, have been broadly based on the use of a single principal metal element, which constitutes at least 50 atomic percent of the overall alloy composition. The alloy properties are then further manipulated by making small additions of other elements. As a result, conventional alloys are generally categorized by the majority host element of which they are composed, as is the case in iron (steel), copper, magnesium, and titanium alloys. Although significant advances in alloy development have taken place in the past 30 years, particular through the use of novel processing techniques such as rapid solidification and mechanical alloying, alloy compositions are still predominantly based on a single-principal-element.

[0005] Research on bulk amorphous alloys has gained considerable interest in recent years. The empirical rules generated for the design of these alloys include 1) the inclusion of at least three elements, 2) an atomic size difference of at least 12% between two of the elements, and 3) a significant negative heat of mixing between the elements. From the published literature related to bulk amorphous alloys, however, one can find that these alloys are still typically based on a single principal element, which has a concentration of at least 40 atomic percent. At least nine different amorphous alloy systems have been developed, which are based on principal elements of titanium, magnesium, copper, iron, cobalt, nickel, platinum, zirconium, and lanthanum.

[0006] In view of the limitations imposed on conventional alloy systems being confined to one or, at most, two principal elements, the inventor, in 1995, put forward a novel, 'multi-principal-element high-entropy alloy' concept. High entropy alloys (HEAs), as these multi-principal-element alloys have been coined, are composed of at least five principal elements, and therefore have a far greater diversity in the possible range of alloy compositions that can be generated. This, in turn, allows an increased number of unique crystal structures, microstructures, and functional uses to be developed. From a thermodynamics perspective, i.e. the theoretical basis of HEA design, the free energy of a multi-principal-element random solution will be considerably lowered by its increased entropy contribution, particularly at elevated temperatures, thereby tending to promote the formation of stable multi-element solution phases in HEAs, as opposed to a, commonly anticipated, mixture of brittle intermetallics.

[0007] As the face-centered cubic (FCC) structure has twelve independent slip systems, it often exhibits better deformation characteristics than other crystal structures. In addition, the FCC structure is well known to retain its hardness to higher temperatures. This is associated to the fact that dislocation motion, i.e. the predominant means of plastic deformation in metallic materials, is less affected by

temperature in an FCC structure, and thus its strength is less sensitive to changes in temperature. It is for these reasons that nickel-, cobalt-, and iron-based superalloys, which possess an FCC crystal structure, operate effectively at elevated temperatures. The raw material costs of these elements goes in the order of cobalt, nickel, and iron; wherein cobalt is the most expensive. The present invention, therefore, provides a novel alloy system that has a reduced cobalt and nickel content, but maintains a matrix with an FCC crystal structure, and thus provides the means to increase the range of industrial applications that can employ materials that operate effectively to elevated temperatures.

SUMMARY OF THE INVENTION

[0008] Through the use of 'multi-principal-element alloy design', a high-temperature resistant multi-principal-element alloy system, which has low Co and Ni contents and possesses an FCC structure, has been invented. The invented alloy is based on a quaternary system of Co, Cr, Fe, and Ni, with the incorporation of at least one other element from Al, Mo, or Ti as the other principal element(s). The contents of Co and Ni are each 20 to 35 atomic percent, and those of Cr and Fe are 12.5 to 20 atomic percent. The sum of Co, Cr, Fe, and Ni is not less than 65 atomic percent. The sum of Al, Mo, and Ti is between 5 and 25 atomic percent. Minor elements, such as Ag, B, C, Cu, Mn, Nb, Ta, Si, V, W, Y, and Zr, can be added to improve the properties of the alloy, but the sum of these minor elements cannot exceed 10 atomic percent. The alloy system can therefore be expressed by the following chemical formula: $(\text{Co}, \text{Cr}, \text{Fe}, \text{Ni})_x \text{M}_y \text{N}_z$, M is Al, Mo, or Ti, or a combination of these. Similarly, N is Ag, B, C, Cu, Mn, Nb, Ta, Si, V, W, Y, or Zr, or a combination of these. It should be noted that the minor elements listed here is not, by any means, exhaustive. The values of x, y and z are ≥ 65 , 5 to 25, and 0 to 10 atomic percent, respectively. The alloy can be cast by conventional methods, for example electrical-resistant wire heating, induction heating, and vacuum arc melting. Furthermore, the alloys may be rapidly quenched from the melt state, or alternatively processed using non-bulk routes, such as mechanical alloying and powder metallurgy. Subsequent to this, the alloys can be subjected to further processing, for instance forging, rolling, and/or thermal homogenization.

[0009] In accordance to the above criteria specifying the preferred embodiment of the invented alloy, eleven HEA specimens were prepared by vacuum arc melting the base elements of $\text{Co}_{1.5}\text{CrFeNi}_{1.5}$ with a suitable addition of Al, Mo, and Ti. The addition of Al, Mo, or Ti was found to enhance properties of the $\text{Co}_{1.5}\text{CrFeNi}_{1.5}$ base alloy to different extents, in which the most to least effective of these elements being in the order of Ti, Mo, and Al.

[0010] A specimen of $\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}_{0.5}$ was then selected from the above eleven alloys to be forged, thermally homogenized, and cold rolled. The changes in its microstructure and hardness at each processing stage were observed. The results indicated that this alloy operates well at elevated temperatures, up to 1100 C, and had good work hardening capabilities.

[0011] A further eleven high-entropy alloy specimens, based on a $\text{Co}_2\text{CrFeNi}_2$ alloy, were also prepared and processed in the same way as described above. The addition of Al, Mo, or Ti was again found to enhance properties of the $\text{Co}_2\text{CrFeNi}_2$ base alloy, with the effectiveness of these elements being in the order of Ti, Mo, then Al. A specimen,

namely $\text{Co}_2\text{CrFeNi}_2\text{Ti}_{0.5}$, was then selected from the above eleven alloys to be forged, thermally homogenized, and cold rolled. The changes in its microstructure and hardness at each processing stage were observed. The results indicated that this alloy, too, operates well at elevated temperatures, up to 1100 C, and had good work hardening capabilities.

[0012] A subsequent eighteen high-entropy alloy specimens with the incorporation of a suitable amount of minor elements, i.e. Ag, B, C, Cu, Mn, Nb, Ta, Si, V, W, Y, Zr, etc., were again processed in the same way as the aforementioned alloys. The sum of the minor elements, in accordance to the preferred embodiment of the invented alloy, does not exceed 10 atomic percent. The hardness of the alloy specimen varied with the addition of the minor elements. Hence, the HEA can be further tailored to meet the requirements for a specific application, in terms of having high-temperature strength, for example, by the addition of minor elements.

[0013] According to another embodiment of the invention, the alloys can be hardened by high-temperature aging after it is cast by vacuum arc melting.

[0014] In conclusion, the invented multi-principal-element high-entropy alloy is a promising material in terms of having good cold working capabilities, undergoing high-temperature age hardening, and exhibiting high-temperature resistance to softening and oxidation. Furthermore, high-entropy alloys are determined to possess relatively simple microstructures, that is, main FCC phase plus some second phases, and can therefore be analyzed effectively by x-ray diffraction and microscopy.

BRIEF DESCRIPTION OF THE DRAWING

[0015] FIG. 1 is a flow chart illustrating the alloy preparation and processing routes according to the preferred embodiments of the invention

DETAILED DESCRIPTION OF THE INVENTION

[0016] Preferred embodiments of the invention will be described in detail with reference to FIG. 1.

[0017] The hardness of the alloy specimens was measured by a Vickers hardness tester (Model MV-1, Matsuzawa Seiki

Co., Ltd.) under a load of 5 kgf, for a loading duration of 15 seconds, and at a rate of 50 $\mu\text{m/s}$. The hardness of each specimen was taken from the mean average of five random hardness measurements. Before the hardness measurements, the surface of each alloy specimen was ground flat by sequentially using #80, #180, #240, #400, #600, #800, and #1200 silicon carbide (SiC) grinding papers.

[0018] The microstructure of the specimens was observed by both optical (OM) and scanning electron microscopes (SEM, JEOL-5410). The composition was analyzed using an energy dispersive spectrometer (EDS). The specimen to be analyzed was cut with a diamond cutter. During cutting, in order to limit the effect of the heat generated from affecting the microstructure, the sample was water cooled. The cut specimens were then ground flat by sequentially using #180, #240, #400, #600, #800, #1200, #2000, and #4000 SiC grinding papers, and underwent a final polishing stage using a 3 μm diamond paste. The polished specimen was then etched using aqua regia ($\text{HNO}_3 + 3\text{HCl}$) in order to facilitate observation of the microstructure.

[0019] The crystal structure of the specimens was evaluated by X-ray diffraction (XRD). The X-ray diffractometer (Rigaku ME510-FM2) employed a Cu target X-ray source operated at 30 kV, 20 mA, producing radiation with a wavelength 1.54056 Å. XRD scans were performed over a scan range of 20 to 100 degrees 2θ , at a scanning speed of 4 degrees/min.

Embodiment 1

[0020] Table 1 shows the compositions of the alloys selected for this embodiment. The specimens, which are labeled HE1 to HE11, are multi-principal-element alloys prepared by adding an appropriate amount of Al, Ti, or Mo to the $\text{Co}_{1.5}\text{CrFeNi}_{1.5}$ base alloy. The base alloy has a Vickers hardness of HV113 and an FCC crystal structure. All of the raw elemental materials have a purity of greater than 99%. Table 2 lists the basic properties of each principal element in these alloys, including their atomic weight, atomic size, melting point, boiling point, density, crystal structure, and the transition temperature of their polymorphs.

TABLE 1

The chemical formula (subscripts in molar fraction) and individual element contents (in atomic percent) for the HE1 to HE11 alloys								
Alloy	Chemical Formula	Element Content in Atomic Percent						
		Co	Cr	Fe	Ni	Al	Ti	Mo
HE1	$\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Al}_{0.5}$	27.3	18.2	18.2	27.3	9.0	—	—
HE2	$\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}_{0.5}$	27.3	18.2	18.2	27.3	—	9.0	—
HE3	$\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Mo}_{0.5}$	27.3	18.2	18.2	27.3	—	—	9.0
HE4	$\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Al}$	25.0	16.7	16.7	25.0	16.6	—	—
HE5	$\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}$	25.0	16.7	16.7	25.0	—	16.6	—
HE6	$\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Mo}$	25.0	16.7	16.7	25.0	—	—	16.6
HE7	$\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Al}_{0.5}\text{Ti}_{0.5}$	25.0	16.7	16.7	25.0	8.3	8.3	—
HE8	$\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Al}_{0.5}\text{Mo}_{0.5}$	25.0	16.7	16.7	25.0	8.3	—	8.3
HE9	$\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}_{0.5}\text{Mo}_{0.5}$	25.0	16.7	16.7	25.0	—	8.3	8.3
HE10	$\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Al}_{0.5}\text{Ti}_{0.5}\text{Mo}_{0.5}$	23.1	15.4	15.4	23.1	7.7	7.7	7.6
HE11	$\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Al}_{0.25}\text{Ti}_{0.5}\text{Mo}_{0.25}$	25.0	16.7	16.7	25.0	4.15	8.3	4.15

TABLE 2

	Properties of constituent elements						
	Element						
	Al	Ti	Co	Cr	Fe	Mo	Ni
Atomic Weight (g/mole)	26.98	47.867	58.93	52.00	55.85	95.94	58.69
Atomic Radius (Å)	1.18	1.76	1.52	1.66	1.56	1.9	1.49
Melting Point (° C.)	660	1668	1495	1907	1538	2623	1455
Boiling Point (° C.)	2519	3287	2927	2671	2861	4639	2913
Density (g/cm ³)	2.70	4.053	8.9	7.14	7.87	10.28	8.91
Crystal Structure (low-temperature)	FCC	HCP	HCP	BCC	BCC	BCC	FCC
Crystal Structure (high-temperature)	FCC	BCC	FCC	FCC	FCC BCC	BCC	FCC
Transition Temperature (° C.)	—	—	417	1840	910 1390	—	—

[0021] FIG. 1 is a flow chart illustrating the preparation and processing of the alloys according to the embodiment of the invention. As shown in FIG. 1, an alloy can be produced in a vacuum arc melting furnace, and subsequently processed by forging, thermal homogenization, rolling, and age hardening. The alloys produced under these various processing routes are then assessed by hardness measurements, XRD, observation of their microstructure, and compositional analysis. Pure metal granules, having a total weight of about 50 grams, were placed in the water-cooled copper hearth for arc melting, and the chamber was then evacuated to a base pressure of 0.01 atm. In order to minimize oxidation, the chamber was purged three times, prior to arc melting, in pure argon gas at a pressure of 0.2 atm. Arc melting was then carried out with an arc current of 500 Amp under an argon atmosphere of 0.26 atm. The ingot was melted evenly and allowed to cool, before it was turned over to be re-melted. This melt process was repeated several times to ensure homogeneity of the cast alloy. The alloy was then cooled and solidified to form the as-cast ingot.

[0022] The crystal structure and hardness of the eleven alloys prepared according to Table 1 have, as shown in Table 3, promising alloy properties. The addition of Al, Mo, and Ti increases the hardness of the base $\text{Co}_{1.5}\text{CrFeNi}_{1.5}$ alloy system, which has a hardness of 113 $\text{HV}_{5.0}$. It is apparent that Ti is the most effective element for enhancing the hardness, whereas Al has the least pronounced effect. Although increasing the amount of each of these elements enhances the hardness, it is found that a BCC phase develops as the second phase. Nevertheless, the principal crystal structure of the alloys is still FCC, and therefore by adding a different amount of these three elements the alloy properties can be adjusted for applications needing, for example, high-temperature strength can be obtained.

TABLE 3

Crystal structure and hardness ($\text{HV}_{5.0}$) of the HE1 to HE11 alloy casts			
Alloy	Composition (atomic ratio)	Crystal Structure	Hardness
HE1	$\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Al}_{0.5}$	FCC	136
HE2	$\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}_{0.5}$	FCC	378
HE3	$\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Mo}_{0.5}$	FCC	193
HE4	$\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Al}$	FCC + BCC	277
HE5	$\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}$	FCC + BCC	581
HE6	$\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Mo}$	FCC + BCC	394

TABLE 3-continued

Crystal structure and hardness ($\text{HV}_{5.0}$) of the HE1 to HE11 alloy casts			
Alloy	Composition (atomic ratio)	Crystal Structure	Hardness
HE7	$\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Al}_{0.5}\text{Ti}_{0.5}$	FCC + BCC	385
HE8	$\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Al}_{0.5}\text{Mo}_{0.5}$	FCC + BCC	200
HE9	$\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}_{0.5}\text{Mo}_{0.5}$	FCC + BCC	417
HE10	$\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Al}_{0.5}\text{Ti}_{0.5}\text{Mo}_{0.5}$	FCC + BCC	561
HE11	$\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Al}_{0.25}\text{Ti}_{0.5}\text{Mo}_{0.25}$	FCC + BCC	383

Embodiment 2

[0023] In accordance with the alloy preparation and processing flow chart, shown in FIG. 1, the HE2 alloy (refer to Table 1 above), with a composition of $\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}_{0.5}$, was heated in an air furnace to a temperature of 1000° C. for 15 minutes, and then subjected to hot forging using a pneumatic forging machine (Model: OT-1521280). Forging was conducted at a load of 250 kg to obtain a reduction of 40% in thickness. Next, the forged specimens were placed in a furnace under ambient atmosphere and homogenized at 1100° C. for 24 hours, after which they either underwent furnace cooling or water quenching. The hardness of the specimens at each stage is given in Table 4. The hardness is increased by about 30% after forging, then decreases after homogenization followed by furnace cooling, but is elevated slightly after homogenization followed by water quenching. This alloy is not found to suffer high-temperature softening, even after treatment at 1100° C., and therefore exhibits excellent high temperature performance. At each stage, only a single FCC phase can be identified from XRD analysis.

TABLE 4

Hardness ($\text{HV}_{5.0}$) of $\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}_{0.5}$ alloy after casting, forging, and homogenizing				
Alloy	As-cast	High-temp Forged	Homogenized and Furnace Cooled	Homogenized and Water Quenched
$\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}_{0.5}$	378	488	313	392

[0024] The change in hardness is given in Table 5 for the homogenized (furnace-cooled) alloy specimen ($\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}_{0.5}$) which underwent further cold rolling for different thickness reductions of 0%, 5%, 15%, 30%, and 80%, respectively on a two-high rolling machine (Model: DBR250). The hardness of the rolled alloy specimen is enhanced with the increasing reduction. The hardness of the sample is seen to increase significantly at a thickness reduction of 30%, where the hardness of the alloy specimen is about 1.78 times higher than that of the original sample (0% reduction). Hence, the alloy displays excellent work hardening behavior. The intensity of the XRD peaks pertaining to the FCC structure of the $\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}_{0.5}$ alloy gradually decreases with increasing reduction. This is a result of the increased lattice distortion for the worked alloy, which causes a decrease in the constructive interference of the diffracted X-ray radiation.

TABLE 5

Hardness (HV _{5.0}) of $\text{Co}_{1.5}\text{CrFeNi}_{1.5}\text{Ti}_{0.5}$ alloy being rolled at different thickness reductions					
	Reduction				
	0%	5%	15%	30%	80%
Hardness	313	467	452	558	545

Embodiment 3

[0025] Table 6 presents the alloy compositions selected for this embodiment. Specimens are labeled HE12 to HE22, and are multi-principal-element alloys prepared by incorporating a suitable amount of Al, Ti, or Mo into a $\text{Co}_2\text{CrFeNi}_2$ base alloy. The hardness of the base alloy is 108 HV_{5.0}, and it possesses an FCC crystal structure. The purity of the elemental raw materials is higher than 99%.

TABLE 6

The chemical formula (subscripts in molar fraction) and individual element contents (in atomic percent) for the HE12 to HE22 alloys								
Alloy	Chemical Formula	Element Content in Atomic Percent						
		Co	Cr	Fe	Ni	Al	Ti	Mo
HE12	$\text{Co}_2\text{CrFeNi}_2\text{Al}_{0.5}$	30.8	15.4	15.4	30.8	7.6	—	—
HE13	$\text{Co}_2\text{CrFeNi}_2\text{Ti}_{0.5}$	30.8	15.4	15.4	30.8	—	7.6	—
HE14	$\text{Co}_2\text{CrFeNi}_2\text{Mo}_{0.5}$	30.8	15.4	15.4	30.8	—	—	7.6
HE15	$\text{Co}_2\text{CrFeNi}_2\text{Al}$	28.6	14.3	14.3	28.6	14.2	—	—
HE16	$\text{Co}_2\text{CrFeNi}_2\text{Ti}$	28.6	14.3	14.3	28.6	—	14.2	—
HE17	$\text{Co}_2\text{CrFeNi}_2\text{Mo}$	28.6	14.3	14.3	28.6	—	—	14.2
HE18	$\text{Co}_2\text{CrFeNi}_2\text{Al}_{0.5}\text{Ti}_{0.5}$	28.6	14.3	14.3	28.6	7.1	7.1	—
HE19	$\text{Co}_2\text{CrFeNi}_2\text{Al}_{0.5}\text{Mo}_{0.5}$	28.6	14.3	14.3	28.6	7.1	—	7.1
HE20	$\text{Co}_2\text{CrFeNi}_2\text{Ti}_{0.5}\text{Mo}_{0.5}$	28.6	14.3	14.3	28.6	—	7.1	7.1
HE21	$\text{Co}_2\text{CrFeNi}_2\text{Al}_{0.5}\text{Ti}_{0.5}\text{Mo}_{0.5}$	26.7	13.3	13.3	26.7	6.7	6.7	6.6
HE22	$\text{Co}_2\text{CrFeNi}_2\text{Al}_{0.25}\text{Ti}_{0.5}\text{Mo}_{0.25}$	28.6	14.3	14.3	28.6	3.6	7.0	3.6

[0026] The crystal structure and hardness of the eleven alloys prepared in this embodiment, as given in Table 6, have, as provided in Table 7, promising alloy properties. The addition of Al, Mo, and Ti increases the hardness of the base $\text{Co}_2\text{CrFeNi}_2$ alloy system. It is apparent that Ti is the most effective element for enhancing the hardness, whereas Al has the least pronounced effect. Although increasing the amount

of each of these elements enhances the hardness, it is found that a BCC phase develops as the second phase. Nevertheless, the principal crystal structure of the alloys is still FCC, and therefore by adding a different amount of these three elements, the alloy properties can be adjusted for applications needing, for example, different high-temperature strength can be obtained.

TABLE 7

Crystal structure and hardness (HV _{5.0}) of alloy casts HE12–HE22			
Alloy	Composition (atomic ratio)	Crystal Structure	Hardness
HE12	$\text{Co}_2\text{CrFeNi}_2\text{Al}_{0.5}$	FCC	124
HE13	$\text{Co}_2\text{CrFeNi}_2\text{Ti}_{0.5}$	FCC	340
HE14	$\text{Co}_2\text{CrFeNi}_2\text{Mo}_{0.5}$	FCC	170
HE15	$\text{Co}_2\text{CrFeNi}_2\text{Al}$	FCC + BCC	230
HE16	$\text{Co}_2\text{CrFeNi}_2\text{Ti}$	FCC + BCC	456
HE17	$\text{Co}_2\text{CrFeNi}_2\text{Mo}$	FCC + BCC	236
HE18	$\text{Co}_2\text{CrFeNi}_2\text{Al}_{0.5}\text{Ti}_{0.5}$	FCC + BCC	356
HE19	$\text{Co}_2\text{CrFeNi}_2\text{Al}_{0.5}\text{Mo}_{0.5}$	FCC + BCC	180
HE20	$\text{Co}_2\text{CrFeNi}_2\text{Ti}_{0.5}\text{Mo}_{0.5}$	FCC + BCC	316
HE21	$\text{Co}_2\text{CrFeNi}_2\text{Al}_{0.5}\text{Ti}_{0.5}\text{Mo}_{0.5}$	FCC + BCC	376
HE22	$\text{Co}_2\text{CrFeNi}_2\text{Al}_{0.25}\text{Ti}_{0.5}\text{Mo}_{0.25}$	FCC + BCC	349

Embodiment 4

[0027] Specimens of HE13 alloy ($\text{Co}_2\text{CrFeNi}_2\text{Ti}_{0.5}$), of Embodiment 3, were heated in an air furnace to a temperature of 1000° C. for 15 minutes, and then subjected to hot forging using a pneumatic forging machine (Model: OT-1521280). Forging was conducted at a load of 250 kg to obtain a thickness reduction of 40%. Next, the forged specimens were placed in a furnace under ambient atmosphere and homogenized at 1100° C. for 24 hours, after which they either underwent furnace cooling or water quenching. The hardness of the specimens at each stage is given in Table 8. The hardness is enhanced by about 28%

after forging, then decreases after homogenization combined with furnace cooling, but is elevated slightly after homogenization combined with water quenching. This alloy is not found to suffer high-temperature softening at 1100° C., and therefore exhibits excellent high temperature performance. At each stage, only a single FCC phase can be identified from XRD analysis.

TABLE 8

Hardness (HV _{5.0}) of Co ₂ CrFeNi ₂ Ti _{0.5} alloy after being cast, forged, and homogenized				
Alloy	As-cast	High-temp Forged	Homogenized and Furnace Cooled	Homogenized and Water Quenched
Co ₂ CrFeNi ₂ Ti _{0.5}	339	421	403	328

[0028] The change in hardness is given in Table 9 for the homogenized (furnace-cooled) alloy specimen (Co₂CrFeNi₂Ti_{0.5}) which underwent further cold rolling for different thickness reductions of 0%, 5%, 15%, 30%, and 70%, respectively on a two-high rolling machine (Model: DBR250). The hardness of the rolled alloy specimen is increased with the increasing reduction. The hardness of the sample is seen to increase significantly at a thickness reduction of 30%, where the hardness of the alloy specimen is about 1.57 times higher than the original sample (0% reduction). Hence, the alloy displays excellent work hardening behavior. The intensity of the XRD peaks pertaining to the FCC structure of the Co₂CrFeNi₂Ti_{0.5} alloy gradually decreases with increasing reduction. This is a result of the

increased lattice distortion for the worked alloy causing a decrease in the constructive interference of the diffracted X-ray radiation.

TABLE 9

Hardness (HV _{5.0}) of Co ₂ CrFeNi ₂ Ti _{0.5} alloy rolled at different thickness reductions					
	Reduction				
	0%	5%	15%	30%	70%
Hardness	328	335	416	515	566

Embodiment 5

[0029] The alloy compositions selected for this embodiment are given in Table 10, with the specimens labeled HE23 to HE40. The eighteen alloys are multi-principal-element alloys prepared by incorporating a suitable amount of at least one minor element, such as Ag, B, C, Cu, Mn, Nb, Ta, Si, V, W, Y, and Zr, to a base alloy having compositions of HE1 to HE9 in Table 1, or HE12 to HE20 in Table 6. The purity of the elemental raw materials is higher than 99%.

TABLE 10

The chemical formula (subscripts in molar fraction) and individual element contents (in atomic percent) for the HE23 to HE40 alloys									
Alloy	Chemical Formula	Element Content in Atomic Percent							Minor Element
		Co	Cr	Fe	Ni	Al	Ti	Mo	
HE23	Co _{1.5} CrFeNi _{1.5} Al _{0.5} Ag _{0.2}	26.3	17.5	17.5	26.3	8.9	—	—	Ag: 3.5
HE24	Co _{1.5} CrFeNi _{1.5} Ti _{0.5} B _{0.1} C _{0.1}	26.3	17.5	17.5	26.3	—	8.9	—	B: 1.75 C: 1.75
HE25	Co _{1.5} CrFeNi _{1.5} Mo _{0.5} Si _{0.2}	26.3	17.5	17.5	26.3	—	—	8.9	Si: 3.5
HE26	Co _{1.5} CrFeNi _{1.5} AlCu _{0.2} Mn _{0.3}	23.1	15.4	15.4	23.1	15.4	—	—	Cu: 3.0 Mn: 4.6
HE27	Co _{1.5} CrFeNi _{1.5} TiNb _{0.1} V _{0.2}	23.8	15.9	15.9	23.8	—	15.8	—	Nb: 1.6 V: 3.2
HE28	Co _{1.5} CrFeNi _{1.5} MoNb _{0.1} V _{0.2} W _{0.3}	22.7	15.1	15.1	22.7	—	—	15.3	Nb: 1.5 V: 3 W: 4.6
HE29	Co _{1.5} CrFeNi _{1.5} Al _{0.5} Ti _{0.5} Ta _{0.2} Zr _{0.1}	23.8	15.9	15.9	23.8	7.9	7.9	—	Ta: 3.2 Zr: 1.6
HE30	Co _{1.5} CrFeNi _{1.5} Al _{0.5} Mo _{0.5} V _{0.2} Y _{0.1}	23.8	15.9	15.9	23.8	7.9	—	7.9	V: 3.2 Y: 1.6
HE31	Co _{1.5} CrFeNi _{1.5} Ti _{0.5} Mo _{0.5} Ta _{0.1} Y _{0.1}	24.2	16.1	16.1	24.2	—	8.1	8.1	Ta: 1.6 Y: 1.6
HE32	Co ₂ CrFeNi ₂ Al _{0.5} Ag _{0.2}	29.8	14.9	14.9	29.8	7.4	—	—	Ag: 3
HE33	Co ₂ CrFeNi ₂ Ti _{0.5} B _{0.1} C _{0.1}	29.8	14.9	14.9	29.8	—	7.4	—	B: 1.5 C: 1.5
HE34	Co ₂ CrFeNi ₂ Mo _{0.5} Si _{0.2}	29.8	14.9	14.9	29.8	—	—	7.4	Si: 3
HE35	Co ₂ CrFeNi ₂ AlCu _{0.2} Mn _{0.3}	26.7	13.3	13.3	26.7	13.3	—	—	Cu: 2.7 Mn: 4.0
HE36	Co ₂ CrFeNi ₂ TiNb _{0.1} V _{0.2}	27.4	13.7	13.7	27.4	—	13.7	—	Nb: 1.4 V: 2.7
HE37	Co ₂ CrFeNi ₂ MoNb _{0.1} V _{0.2} W _{0.3}	26.3	13.2	13.2	26.3	—	—	13.2	Nb: 1.3 V: 2.6 W: 3.9
HE38	Co ₂ CrFeNi ₂ Al _{0.5} Ti _{0.5} Ta _{0.2} Zr _{0.1}	27.4	13.7	13.7	27.4	6.8	6.8	—	Ta: 2.8 Zr: 1.4
HE39	Co ₂ CrFeNi ₂ Al _{0.5} Mo _{0.5} V _{0.2} Y _{0.1}	27.4	13.7	13.7	27.4	6.8	—	6.8	V: 2.8 Y: 1.4
HE40	Co ₂ CrFeNi ₂ Ti _{0.5} Mo _{0.5} Ta _{0.1} Y _{0.1}	27.8	13.9	13.9	27.8	—	6.9	6.9	Ta: 1.4 Y: 1.4

[0030] The crystal structure and hardness of the eighteen alloys prepared according to Table 10 are given in Table 11, and convey that these alloys have promising alloy properties. The hardness varies with the addition of the minor elements, as seen in Table 11. By comparing the results of Tables 3, 7 and 11, it can be observed that, apart from Ag and Cu, the addition of other minor elements enhances the hardness. Although the addition of some of the elements increases the formation of a BCC phase, the principal phase is still FCC. Therefore, by using a suitable amount(s) or a specific type(s) of minor element(s), the alloy properties can be adjusted for applications needing, for example, different high-temperature strength can be obtained.

TABLE 11

Crystal structure and hardness (HV _{5.0}) of the alloy casts HE23–HE40			
Alloy	Composition (atomic ratio)	Crystal Structure	Hardness
HE23	Co _{1.5} CrFeNi _{1.5} Al _{0.5} Ag _{0.2}	FCC	125
HE24	Co _{1.5} CrFeNi _{1.5} Ti _{0.5} B _{0.1} C _{0.1}	FCC + boride and carbide	424
HE25	Co _{1.5} CrFeNi _{1.5} Mo _{0.5} Si _{0.2}	FCC + BCC	231
HE26	Co _{1.5} CrFeNi _{1.5} AlCu _{0.2} Mn _{0.3}	FCC + BCC	257
HE27	Co _{1.5} CrFeNi _{1.5} TiNb _{0.1} V _{0.2}	FCC + BCC	715
HE28	Co _{1.5} CrFeNi _{1.5} MoNb _{0.1} V _{0.2} W _{0.3}	FCC + BCC	732
HE29	Co _{1.5} CrFeNi _{1.5} Al _{0.5} Ti _{0.5} Ta _{0.2} Zr _{0.1}	FCC + BCC	590
HE30	Co _{1.5} CrFeNi _{1.5} Al _{0.5} Mo _{0.5} V _{0.2} Y _{0.1}	FCC + BCC	271
HE31	Co _{1.5} CrFeNi _{1.5} Ti _{0.5} Mo _{0.5} Ta _{0.1} Y _{0.1}	FCC + BCC	626
HE32	Co ₂ CrFeNi ₂ Al _{0.5} Ag _{0.2}	FCC	110
HE33	Co ₂ CrFeNi ₂ Ti _{0.5} B _{0.1} C _{0.1}	FCC + boride and carbide	356
HE34	Co ₂ CrFeNi ₂ Mo _{0.5} Si _{0.2}	FCC	177
HE35	Co ₂ CrFeNi ₂ AlCu _{0.2} Mn _{0.3}	FCC + BCC	201
HE36	Co ₂ CrFeNi ₂ TiNb _{0.1} V _{0.2}	FCC + BCC	529
HE37	Co ₂ CrFeNi ₂ MoNb _{0.1} V _{0.2} W _{0.3}	FCC + BCC	580
HE38	Co ₂ CrFeNi ₂ Al _{0.5} Ti _{0.5} Ta _{0.2} Zr _{0.1}	FCC + BCC	556
HE39	Co ₂ CrFeNi ₂ Al _{0.5} Mo _{0.5} V _{0.2} Y _{0.1}	FCC + BCC	229
HE40	Co ₂ CrFeNi ₂ Ti _{0.5} Mo _{0.5} Ta _{0.1} Y _{0.1}	FCC + BCC	503

[0031] According to another embodiment of the invention, the as-cast Co_{1.5}CrFeNi_{1.5}Ti_{0.5} alloy specimens were hardened by a high-temperature aging process. The cast specimens were placed in a furnace and treated at temperatures of 400° C., 600° C., and 800° C. for aging times of 1, 2, 5, and 10 hours. The results are shown in Table 12. A rare high-temperature age hardening phenomenon can be observed at 800° C., especially after a duration of 5 hours, for which the hardness of the alloy increased from 378 to 513HV_{5.0}. After 10 hours the hardness is about 1.33 times better than that of the as-cast specimen (i.e. the specimen that was not aged).

TABLE 12

Alloy hardness (HV _{5.0}) as a function of aging temperature and duration					
Temp.	Time				
	0 hr	1 hr	2 hr	5 hr	10 hr
400° C.	378 ± 10.0	388 ± 3.8	408 ± 9.1	362 ± 4.2	382 ± 5.9
600° C.	378 ± 10.0	400 ± 2.3	387 ± 6.5	384 ± 12.2	387 ± 10.5
800° C.	378 ± 10.0	470 ± 7.7	485 ± 6.1	513 ± 4.1	503 ± 7.0

[0032] It is understood from the aforementioned description that the invented alloy system can be expressed as (Co, Cr, Fe, Ni)_xM_yN_z, where M is at least one element selected from Al, Mo, and Ti, and N is at least one minor element

selected from Ag, B, C, Cu, Mn, Nb, Ta, Si, V, W, Y, and Zr. The values of x, y and z are ≥65, 5 to 25, and 0 to 10 atomic percent, respectively. The Co and Ni elements both have contents from 20 to 35 atomic percent, and those of Cr and Fe is 12.5 to 20 atomic percent.

[0033] The alloy systems all possess a principal FCC phase. As the FCC phase has twelve independent slip systems, it is easy to slip and deform, and therefore it has good ductility. Furthermore, the strength of an FCC structure is well known to be retained to high temperatures. Thus, by the suitable adjustment of the alloy composition, the presently invented multi-principal-element alloys, with an FCC structure as the matrix, can be tailored to have different ranges of strength, and be operated at room or high-temperatures, depending on their applications. Furthermore, as the invented alloys contain at least 12.5 atomic percent of Cr, and at least 20 atomic percent of both Co and Ni, they should have improved corrosion and oxidation resistance. Thus, the alloy should, in principle, be resistant to corrosion and oxidization in high-temperature environments. In addition, since the amount of Co in the alloy is less than 35 atomic percent, the cost is relatively low compared to the present Co-based metal alloys, which have Co contents of at least 50 atomic percent. Hence, the invention utilizes the concept of multi-principal-element alloy design to develop an alloy system that is novel, inventive, cost effective, and industrially applicable.

[0034] While the invention has been described by means of examples, and in terms of the preferred embodiments, it is to be understood that the invention is not limited to the disclosed embodiments. To the contrary, it is intended to cover various modifications and similar arrangements as would be apparent to those skilled in the art. For example, the processing steps in FIG. 1—forging, thermal homogenization, rolling, and age hardening—are for an illustrative purpose, and are therefore not only limited to the sequence described. For instance, in some cases, just one or a combination of the steps will need to be carried out. Therefore, the scope of the appended claims should be accorded the broadest interpretation so as to encompass all such modifications and similar arrangements.

1. A novel high-temperature resistant multi-principal-element alloy, with low cobalt and nickel contents, being described by the following chemical formula:

(Co, Cr, Fe, Ni)_xM_yN_z, for which:

x ≥ 65 atomic percentage, wherein the elemental contents of Co and Ni are each 20 to 35 atomic percent, and the elemental contents of Cr and Fe are each 12.5 to 20 atomic percent;

5 ≤ y ≤ 25 atomic percent, wherein M is one, or a combination of Al, Mo, and Ti; and

0 < z ≤ 10 atomic percent, wherein N is one, or a combination of Ag, B, C, Cu, Mn, Nb, Ta, Si, V, W, Y, and Zr.

wherein the hardness of the alloy increases with increasing thickness reduction of the alloy caused by working on the alloy, and the hardness of the alloy increases as the alloy is age hardened at a temperature over 400° C.

2. The novel high-temperature resistant alloy, with low contents of cobalt and nickel, as described in claim 1, wherein the alloy is cast by vacuum arc melting.

3. The novel high-temperature resistant alloy, with low contents of cobalt and nickel, as described in claim 1 or 2,

wherein the alloy possesses a predominant face-centered cubic matrix.

4. The novel high-temperature resistant alloy, with low contents of cobalt and nickel, as described in claim 1 or 2, wherein the alloy is worked by forging.

5. The novel high-temperature resistant alloy, with low contents of cobalt and nickel, as described in claim 1 or 2, wherein the alloy is processed by thermal homogenization.

6. The novel high-temperature resistant alloy, with low contents of cobalt and nickel, as described in claim 1 or 2, wherein the alloy is worked by rolling.

7. The novel high-temperature resistant alloy, with low contents of cobalt and nickel, as described in claim 1 or 2, wherein the alloy is processed by aging hardening.

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