Abstract: Embodiments of high entropy alloys which can contain non-high entropy second phases. The high entropy alloys can include a number of different principle elements which can form relatively simple structures, such as FCC or BCC. The high entropy alloys can also include secondary phases such as intermetallics, laves phases, carbide, borides, borocarbides, nitrides, silicides, aluminides, oxides, phosphides, phosphates, sulfides, sulfates, hydrides, hydrates, and carbonitrides.

FIG. 2E
Published:

— with international search report (Art. 21(3))
HIGH ENTROPY ALLOYS WITH NON-HIGH ENTROPY SECOND PHASES

INTEGRATION BY REFERENCE TO ANY PRIORITY APPLICATIONS

[0001] This Application claims from the benefit of U.S. Provisional Application No. 62/101,798, filed January 9, 2015, titled "HIGH ENTROPY ALLOYS WITH NON-HIGH ENTROPY SECOND PHASES," the entirety of which is incorporated herein by reference.

BACKGROUND

Field

[0002] This disclosure relates to high entropy materials and the use of "non-high-entropy" second phase strengthening.

SUMMARY

[0003] Disclosed herein are embodiments of a strengthened high entropy alloy comprising a high entropy matrix as defined by a FCC structure, a BCC structure, or a combination of both, wherein the high entropy matrix comprises at least three principal elements each comprising between 5 and 90 wt.% of the matrix and one or more secondary non-high entropy phases.

[0004] In some embodiments, the high entropy matrix can comprise at least three principal elements each comprising between 5 and 50 wt.% of the matrix. In some embodiments, the high entropy matrix can comprise at least three principal elements each comprising between 5 and 35 wt.% of the matrix.

[0005] In some embodiments, the secondary non-high entropy phases can be selected from the group consisting of intermetallics, laves phases, carbide, borides, borocarbides, nitrides, silicides, aluminides, oxides, phosphides, phosphates, sulfides, sulfates, hydrides, hydrates, and carbonitrides.

[0006] In some embodiments, the secondary non-high entropy phase can comprise at least 1% of the volume fraction of the alloy. In some embodiments, the one or more secondary non-high entropy phase can comprise at least 5% of the volume fraction of the
alloy. In some embodiments, the one or more secondary non-high entropy phase can comprise at least 20% of the volume fraction of the alloy.

[0007] In some embodiments, the high entropy matrix can comprise 4 or more principal elements. In some embodiments, the high entropy matrix can comprise 5 or more principal elements. In some embodiments, the alloy can comprise W_{20}Ta_{16}Nb_{24}Mo_{20}Vi_{8}C_{2}.

[0008] Also disclosed herein are embodiments of a multi-component alloy having both high and non-high entropy phases, the alloy forming a material comprising a high entropy matrix formed from at least three principle elements, the high entropy matrix comprising either one or two simple structures, and at least one secondary non-high entropy phases, wherein the high entropy matrix is embedded with the at least one secondary non-high entropy phases. In some embodiments, the one or two simple structures can be an FCC structure, a BCC structure, or combinations thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] Figures 1A-C shows an embodiment of a high entropy alloy.


DETAILED DESCRIPTION

[0011] In embodiments of this disclosure, several techniques are described for improvement on the properties of high entropy alloys. High entropy alloys are a unique class of material with a unique set of useful properties, such as high strength (in some cases above 600 MPa), especially at elevated temperatures (such as temperatures above 1400°C). High entropy alloys are conventionally defined as alloys which are composed of solely 1 or 2 simple structures, such as FCC, BCC or a combination of the two, as opposed to a multi-phase structures, which is typically seen in conventional high alloy materials. Further, by conventional definition, high entropy alloys can be described as those with 3, 4, or 5 or more principal elements. A principal element can be between 5 and 35 wt.% (or about 5 to about 35 wt. %).

[0012] The tendency to form a simple structure in high entropy alloys can be accurately predicted by calculating the enthalpy of mixing (\(\Delta H_{\text{mix}}\)), the entropy of mixing
(ASmix), and the atomic size difference (δ) between the elements for a given alloy composition. In high entropy alloys, the following conditions can be met simultaneously, -22 ≤ AHmix ≤ 7 kJ/mol (or about -22 ≤ ΔH mix ≤ about 7 kJ/mol), δ ≤ 8.5 (or ≤ about 8.5), and 11 ≤ ΔS mix < 19.5 J/(K mol) (or about 11 ≤ ΔS mix ≤ about 19.5 J/(K mol)).

Embodiments of the technology disclosed herein relate to alloys which contain a high entropy matrix embedded with a second phase to further increase performance.

As disclosed herein, the term alloy can refer to the chemical composition of powder used to form a desired component, the powder itself (such as feedstock), the composition of a metal component formed, for example, by the heating and/or deposition of the powder, and the metal component itself.

Embodiments of the disclosed technology are a unique alloy class wherein second phase non 'high entropy' phases can be formed in the microstructure while the remaining matrix remains a high entropy alloy. The disclosed alloy class is not inherent or obvious in that the definition of a high entropy alloy is one that contains only one or two simple structures. The simultaneous growth of additional phases and the retention of a high entropy matrix is not inherent or obvious, and may be obtained with the use of specialized computational metallurgy techniques.

In some embodiments, the high entropy matrix can be composed of 3 or more principal elements. In some embodiments, the high entropy matrix can be composed of 4 or more principal elements. In some embodiments, the high entropy matrix can be composed of 5 or more principal elements.

In some embodiments, the high entropy matrix alloying elements each can range in weight from 5% to 90% (or about 5% to about 90%). In some embodiments, the high entropy matrix alloying elements each can range in weight from 5% to 50% (or about 5% to about 50%). In some embodiments, the high entropy matrix alloying elements each can range in weight from 5% to 35% (or about 5% to about 35%).

Additional embodiments pertain to the second (non-high entropy) phases of the alloys. Any phase which is not a high entropy phase can be considered a non-high entropy phase. In some embodiments, the additional phases can be one or more of the following: intermetallics, laves phases, carbide, borides, borocarbides, nitrides, silicides,
aluminides, oxides, phosphides, phosphates, sulfides, sulfates, hydrides, hydrates, or carbonitrides.

[0018] In some embodiments, the non-high entropy phase fraction can be at or above 1% volume fraction (or at or above about 1% volume fraction). In some embodiments, the non-high entropy phase fraction can be at or above 5% volume fraction (or at or above about 5% volume fraction). In some embodiments, the non-high entropy phase fraction can be at or above 20% volume fraction (or at or above about 20% volume fraction).

Examples:

[0019] An example of a high entropy alloy is shown in Figures 1A-C for a \( \text{W}_2\text{O}_{15}\text{Ta}_6\text{Nb}_{24}\text{Mo}_2\text{O}_{15}\text{V}_2\text{O} \) alloy. The thermodynamic diagram of Figure 1B [101] shows that this multi-component alloy forms one single simple BCC phase. A simple BCC phase was confirmed in the microstructure [103] shown in Figure 1A and XRD diffraction spectrum of Figure 1C [104] of the produced alloy.

[0020] This alloy was then selected as the base for further alloying additions in order to create a high entropy matrix strengthened with non-high entropy second phases. In this particular example, carbon was added with the intention of producing carbides. The calculated thermodynamic results and experimental analysis for this alloy, \( \text{W}_2\text{O}_{15}\text{Ta}_6\text{Nb}_{24}\text{Mo}_2\text{O}_{15}\text{V}_2\text{O}8\text{C}_2 \) is shown in Figures 2A-E. The thermodynamic calculations [201] of Figure 2E show that the alloy now forms two phases, 1) a high entropy matrix [202] and 2) a niobium-vanadium carbide [203]. The matrix is still a high entropy alloy in that it forms a single simple BCC structure containing 5 elements each in high weight fraction. However, in this example, the matrix is further strengthened by the presence of a non-high-entropy niobium-vanadium carbide, as a second phase at approx. 40 mole fraction. This thermodynamic prediction was confirmed with microscopy [204] as shown in Figures 2A-C and X-ray diffractometry [205] as shown in Figure 2D.

Applications and processes for use:

[0021] The alloys described in this patent can be used in a variety of applications and industries. Some non-limiting examples of applications of use include:
[0022] Surface Mining applications include the following components and coatings for the following components: Wear resistant sleeves and/or wear resistant hardfacing for slurry pipelines, mud pump components including pump housing or impeller or hardfacing for mud pump components, ore feed chute components including chute blocks or hardfacing of chute blocks, separation screens including but not limited to rotary breaker screens, banana screens, and shaker screens, liners for autogenous grinding mills and semi-autogenous grinding mills, ground engaging tools and hardfacing for ground engaging tools, wear plate for buckets and dumptruck liners, heel blocks and hardfacing for heel blocks on mining shovels, grader blades and hardfacing for grader blades, stacker reclaimers, sizer crushers, general wear packages for mining components and other comminution components.

[0023] Downstream oil and gas applications include the following components and coatings for the following components: Downhole casing and downhole casing, drill pipe and coatings for drill pipe including hardbanding, mud management components, mud motors, fracking pump sleeves, fracking impellers, fracking blender pumps, stop collars, drill bits and drill bit components, directional drilling equipment and coatings for directional drilling equipment including stabilizers and centralizers, blow out preventers and coatings for blow out preventers and blow out preventer components including the shear rams, oil country tubular goods and coatings for oil country tubular goods.

[0024] Upstream oil and gas applications include the following components and coatings for the following components: Process vessels and coating for process vessels including steam generation equipment, amine vessels, distillation towers, cyclones, catalytic crackers, general refinery piping, corrosion under insulation protection, sulfur recovery units, convection hoods, sour stripper lines, scrubbers, hydrocarbon drums, and other refinery equipment and vessels.

[0025] Pulp and paper applications include the following components and coatings for the following components: Rolls used in paper machines including yankee dryers and other dryers, calendar rolls, machine rolls, press rolls, digesters, pulp mixers, pulpers, pumps, boilers, shredders, tissue machines, roll and bale handling machines, doctor blades, evaporators, pulp mills, head boxes, wire parts, press parts, M.G. cylinders, pope reels, winders, vacuum pumps, deflakers, and other pulp and paper equipment,
Power generation applications include the following components and coatings for the following components: boiler tubes, precipitators, fireboxes, turbines, generators, cooling towers, condensers, chutes and troughs, augers, bag houses, ducts, ID fans, coal piping, and other power generation components.

Agriculture applications include the following components and coatings for the following components: chutes, base cutter blades, troughs, primary fan blades, secondary fan blades, augers and other agricultural applications.

Construction applications include the following components and coatings for the following components: cement chutes, cement piping, bag houses, mixing equipment and other construction applications.

Machine element applications include the following components and coatings for the following components: Shaft journals, paper rolls, gear boxes, drive rollers, impellers, general reclamation and dimensional restoration applications and other machine element applications.

Steel applications include the following components and coatings for the following components: cold rolling mills, hot rolling mills, wire rod mills, galvanizing lines, continue pickling lines, continuous casting rolls and other steel mill rolls, and other steel applications.

The alloys described in this patent can be produced and or deposited in a variety of techniques effectively. Some non-limiting examples of processes include:

Thermal spray process including those using a wire feedstock such as twin wire arc, spray, high velocity arc spray, combustion spray and those using a powder feedstock such as high velocity oxygen fuel, high velocity air spray, plasma spray, detonation gun spray, and cold spray. Wire feedstock can be in the form of a metal core wire, solid wire, or flux core wire. Powder feedstock can be either a single homogenous alloy or a combination of multiple alloy powder which result in the desired chemistry when melted together.

Welding processes including those using a wire feedstock including but not limited to metal inert gas (MIG) welding, tungsten inert gas (TIG) welding, arc welding, submerged arc welding, open arc welding, bulk welding, laser cladding, and those using a powder feedstock including but not limited to laser cladding and plasma transferred arc...
welding. Wire feedstock can be in the form of a metal core wire, solid wire, or flux core wire. Powder feedstock can be either a single homogenous alloy or a combination of multiple alloy powder which result in the desired chemistry when melted together.

[0034] Casting processes including processes typical to producing cast iron including but not limited to sand casting, permanent mold casting, chill casting, investment casting, lost foam casting, die casting, centrifugal casting, glass casting, slip casting and process typical to producing wrought steel products including continuous casting processes.

[0035] Post processing techniques including but not limited to rolling, forging, surface treatments such as carburizing, nitriding, carbonitriding, heat treatments including but not limited to austenitizing, normalizing, annealing, stress relieving, tempering, aging, quenching, cryogenic treatments, flame hardening, induction hardening, differential hardening, case hardening, decarburization, machining, grinding, cold working, work hardening, and welding.

[0036] From the foregoing description, it will be appreciated that an inventive alloys are disclosed. While several components, techniques and aspects have been described with a certain degree of particularity, it is manifest that many changes can be made in the specific designs, constructions and methodology herein above described without departing from the spirit and scope of this disclosure.

[0037] Certain features that are described in this disclosure in the context of separate implementations can also be implemented in combination in a single implementation. Conversely, various features that are described in the context of a single implementation can also be implemented in multiple implementations separately or in any suitable subcombination. Moreover, although features may be described above as acting in certain combinations, one or more features from a claimed combination can, in some cases, be excised from the combination, and the combination may be claimed as any subcombination or variation of any subcombination.

[0038] Moreover, while methods may be depicted in the drawings or described in the specification in a particular order, such methods need not be performed in the particular order shown or in sequential order, and that all methods need not be performed, to achieve desirable results. Other methods that are not depicted or described can be incorporated in the
example methods and processes. For example, one or more additional methods can be performed before, after, simultaneously, or between any of the described methods. Further, the methods may be rearranged or reordered in other implementations. Also, the separation of various system components in the implementations described above should not be understood as requiring such separation in all implementations, and it should be understood that the described components and systems can generally be integrated together in a single product or packaged into multiple products. Additionally, other implementations are within the scope of this disclosure.

[0039] Conditional language, such as "can," "could," "might," or "may," unless specifically stated otherwise, or otherwise understood within the context as used, is generally intended to convey that certain embodiments include or do not include, certain features, elements, and/or steps. Thus, such conditional language is not generally intended to imply that features, elements, and/or steps are in any way required for one or more embodiments.

[0040] Conjunctive language such as the phrase "at least one of X, Y, and Z," unless specifically stated otherwise, is otherwise understood with the context as used in general to convey that an item, term, etc. may be either X, Y, or Z. Thus, such conjunctive language is not generally intended to imply that certain embodiments require the presence of at least one of X, at least one of Y, and at least one of Z.

[0041] Language of degree used herein, such as the terms "approximately," "about," "generally," and "substantially" as used herein represent a value, amount, or characteristic close to the stated value, amount, or characteristic that still performs a desired function or achieves a desired result. For example, the terms "approximately", "about", "generally," and "substantially" may refer to an amount that is within less than or equal to 10% of, within less than or equal to 5% of, within less than or equal to 1% of, within less than or equal to 0.1% of, and within less than or equal to 0.01% of the stated amount. If the stated amount is 0 (e.g., none, having no), the above recited ranges can be specific ranges, and not within a particular % of the value. For example, within less than or equal to 10 wt./vol. % of, within less than or equal to 5 wt./vol. % of, within less than or equal to 1 wt./vol. % of, within less than or equal to 0.1 wt./vol. % of, and within less than or equal to 0.01 wt./vol. % of the stated amount.
Some embodiments have been described in connection with the accompanying drawings. The figures are drawn to scale, but such scale should not be limiting, since dimensions and proportions other than what are shown are contemplated and are within the scope of the disclosed inventions. Distances, angles, etc. are merely illustrative and do not necessarily bear an exact relationship to actual dimensions and layout of the devices illustrated. Components can be added, removed, and/or rearranged. Further, the disclosure herein of any particular feature, aspect, method, property, characteristic, quality, attribute, element, or the like in connection with various embodiments can be used in all other embodiments set forth herein. Additionally, it will be recognized that any methods described herein may be practiced using any device suitable for performing the recited steps.

While a number of embodiments and variations thereof have been described in detail, other modifications and methods of using the same will be apparent to those of skill in the art. Accordingly, it should be understood that various applications, modifications, materials, and substitutions can be made of equivalents without departing from the unique and inventive disclosure herein or the scope of the claims.
WHAT IS CLAIMED IS:

1. A strengthened high entropy alloy comprising:
   a high entropy matrix as defined by a FCC structure, a BCC structure, or a combination of both, wherein the high entropy matrix comprises at least three principal elements each comprising between 5 and 90 wt.% of the matrix; and
   one or more secondary non-high entropy phases.

2. The alloy of claim 1, wherein the high entropy matrix comprises at least three principal elements each comprising between 5 and 50 wt.% of the matrix.

3. The alloy of claim 1, wherein the high entropy matrix comprises at least three principal elements each comprising between 5 and 35 wt.% of the matrix.

4. The alloy of claim 1, wherein the one or more secondary non-high entropy phases is selected from the group consisting of intermetallics, laves phases, carbide, borides, borocarbides, nitrides, silicides, aluminides, oxides, phosphides, phosphates, sulfides, sulfates, hydrides, hydrates, and carbonitrides.

5. The alloy of claim 1, wherein the one or more secondary non-high entropy phase comprises at least 1% of the volume fraction of the alloy.

6. The alloy of claim 1, wherein the one or more secondary non-high entropy phase comprises at least 5% of the volume fraction of the alloy.

7. The alloy of claim 1, wherein the one or more secondary non-high entropy phase comprises at least 20% of the volume fraction of the alloy.

8. The alloy of claim 1, wherein the high entropy matrix comprises 4 or more principal elements.
9. The alloy of claim 1, wherein the high entropy matrix comprises 5 or more principal elements.

10. The alloy of claim 1, wherein the alloy comprises $W_2OTa_iO_2Nb_{2i}Mo_{2i}O_2Vi_8C_2$.

11. A multi-component alloy having both high and non-high entropy phases, the alloy forming a material comprising:

   a high entropy matrix formed from at least three principle elements, the high entropy matrix comprising either one or two simple structures; and

   at least one secondary non-high entropy phases;

   wherein the high entropy matrix is embedded with the at least one secondary non-high entropy phases.

12. The alloy of Claim 11, wherein the one or two simple structures are an FCC structure, a BCC structure, or combinations thereof.
Refractory High Entropy Alloy

FIG. 1A

FIG. 1B

Mole Fractions of Phases

W20-Ta16-Nb24-Mo20-V20
HEA Alloy by wt. %

Temperature (K)
Refractory High Entropy Alloy

Measured Rockwell C Hardness = 40

FIG. 1C
Refractory High Entropy Alloy + Carbide Strengthening

**FIG. 2A**

As-Cast (Low Magnification)

**FIG. 2B**

As-Cast (High Magnification)

**FIG. 2C**

Homogenized (High Magnification)
Refractory High Entropy Alloy + Carbide Strengthening

Measured Rockwell C Hardnes = 57

FIG. 2D

FIG. 2E
INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2016/012519

A. CLASSIFICATION OF SUBJECT MATTER

IPCI(8) - C22C 30/00 (2016.01)
CPC - C22C 30/00 (2016.02)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPCI(8) - C01B 6/00; C22C 28/00, 29/00, 30/00, 30/02, 30/04, 30/06 (2016.01)
CPC - C01B 6/00, 6/246; C22C 28/00, 29/00, 30/00, 30/02, 30/04, 30/06, 45/10 (2016.02)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

USPC - 145/501, 505; 420/580, 581, 591 (keyword delimited)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

PatentScope, Google Patents, Google Scholar, Google

Search terms used: high entropy alloy, HEA, matrix, FCC, BCC, structure, elements, secondary phase, non-high entropy, weight percent

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>US 2013/0108502 A1 (BEI) 02 May 2013 (02.05.2013) entire document</td>
<td>1-12</td>
</tr>
<tr>
<td>A</td>
<td>US 2010/0132408 A1 (BILLIERES) 03 June 2010 (03.06.2010) entire document</td>
<td>1-12</td>
</tr>
</tbody>
</table>

Further documents are listed in the continuation of Box C.

See patent family annex.

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

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"&" document member of the same patent family

Date of the actual completion of the international search

08 March 2016

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