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(54) HIGH WEAR RESISTANT HIGH ENTROPY ALLOY AND PREPARATION THEREOF

(57) The present invention discloses high entropy alloys that consist of the following composition, wherein the percentages are expressed by weight with respect to the total weight of the alloy: 5-20wt.% Cr, 10-25wt.% Mn, 0.3-20wt.% Si, 0.2-6wt.% Fe and the balance Ni and unavoidable impurities. The invention also discloses a process for manufacturing these high entropy alloys with high hardness values. The invention also comprises submitting the alloys to a thermal treatment and achieving an improved hardness and very good corrosion resistance. Finally, the invention refers to the uses of these alloys for manufacturing parts for use for example cutting tools, high temperature heat exchange applications and high wear resistance components in machinery for construction and mining.

EP 3 670 684 A1

Description

FIELD OF THE INVENTION

[0001] The present invention is encompassed within the sector of metallurgical industry. Particularly, it relates to a new high entropy alloy with a good balance between corrosion resistance and wear resistance, useful in different applications such as cutting tools, high temperature heat exchange applications and high wear resistance components in machinery for construction and mining. The high entropy alloy comprises a dual microstructure. This alloy may be submitted to a hardening heat treatment by which its hardness is improved proportionally to the quantity of one of the main chemical elements (Si). The present invention also relates to a method for its preparation and to the casting of it for manufacturing parts for use in diverse industries.

BACKGROUND OF THE INVENTION

[0002] Tool steels, manganese steels and white cast iron are currently used alloys to achieve high wear resistant properties by different microstructure related aspects. Tool steels are high alloyed steels with the main requirement of high hardness which are used to build up hand tools or cutting tools mainly for machining. Manganese steels have between 5 and 15 wt.% of manganese, and these are used for manufacturing mining wear resisting elements such as shot blasting cabins, mills and drills. White cast iron are high carbon content alloys with 1.8-4 wt.% carbon and 10-20 wt.% chrome and are used in high wear resisting elements for use in similar applications than the manganese steels. In the case of tool steels and white cast iron, their hardening is achieved by the generation of carbides, whereas in the case of manganese steel hardening is achieved by cold deformation. All these alloys are used in applications where high wear resistance is required. Nevertheless, although they present quite good wear resistance for these applications, they show poor corrosion resistance in comparison to AISI alloy. Thus, they are not adequate for use in hazardous environmental conditions.

[0003] Tool steels, manganese steels and white cast iron may be submitted to an annealing heat treatment at about 700-1000 °C to increase their toughness. However, when components of tool steel, manganese steel or white cast iron are submitted to a hardening heat treatment, cracks are prone to appear in the component due to their low ductility and the high stresses accumulated because of the high cooling speed required in the heat treatment process, to avoid perlite and carbides formation. This crack generation reduces their service life significantly.

[0004] In view of all these shortcomings, there is the need in the state of the art to provide new alloys that have high hardness values and wear resistance combined with a good corrosion resistance.

DESCRIPTION OF THE DRAWINGS

[0005]

Figure 1: Scanning Electron Microscope (SEM) image of the high entropy alloy VI as cast, prepared as described in Example 1, showing its microstructure.

Figure 2: SEM image of the high entropy alloy VI after heat treatment as described in Example 4 ii), showing its microstructure.

Figure 3: Energy Dispersive Spectrometer (EDS) composition analysis of the dark grey phase of alloy VI shown in Figure 1.

Figure 4: Energy Dispersive Spectrometer (EDS) composition analysis of the light grey phase of alloy VI shown in Figure 1.

Figure 5: Hardness evolution of some exemplary alloys of the invention as cast and after heat treatment characterized by increasing amounts of Silicon in their chemical compositions.

Figure 6: Images showing the result of submitting to 648 hours of salt spray test: a) one sample of AISI 347; b) one sample of alloy VI heat-treated and c) one sample of alloy V heat-treated d) one sample of alloy 1.2842 submitted in this case to only 48 hours of salt spray test.

DESCRIPTION OF THE INVENTION

[0006] High entropy alloys are well known alloys with solid solution hardening mechanism of different elements in the range of near to equiatomic proportion minimizing the quantity of different phases.

[0007] The present disclosure provides new high entropy alloys as cast and new high entropy alloys after their heat treatment, methods for their preparation and their use as defined in the appending claims. Examples of these alloys are presented in figure 5 (for example: alloy V is equivalent in atomic proportion to $Cr_{0.5}MnSiNi_2$ and alloy VI equivalent to

$Cr_{0.5}MnSi_{0.75}Ni_2$)

[0008] The high entropy alloys of the present invention show advantageously high hardness and high wear resistance, and at the same time also good corrosion resistance. The high entropy alloys of the invention withstand, for example, working conditions in high wear requiring operations in mines, or working conditions of cutting tools and hand tools in construction. The alloys are also able to withstand these extreme working conditions in the presence of corrosive solutions, such as salt water, acid and basic environments in general.

[0009] In the context of the present invention, and unless otherwise stated, the indicated Vickers hardness values correspond to surface or nucleus hardness values, measured according to the method described under Examples. Also percentages are always, unless otherwise stated, expressed by weight with respect to the total weight of the alloy.

[0010] A high entropy alloy as cast is herein disclosed which consists of the following chemical composition in weight percent:

Cr:	5.0 - 20wt.%
Mn:	10.0 - 25wt.%
Si:	0.3 - 20wt.%
Fe:	0.2 - 6wt.%

the balance being Ni and unavoidable impurities.

[0011] Among the unavoidable impurities P and S can be mentioned, which, when present are in contents of equal or less than 0.03 wt.% each.

[0012] This high entropy alloy as cast of the invention comprises a dual microstructure conformed by two different FCC (Face Center Cubic) phases that can be seen with different colour: dark grey and light grey in scanning electron microscope (SEM), and which will be hereinafter referred to as the dark grey phase and the light grey phase.

[0013] Their crystallographic structure (obtained by X-ray diffraction (DRX)) is described in the following, comprising a different cell parameter:

Phase	System	Spatial group	Cell parameter (Å)
Light grey phase	Cubic	Face centered	3.59
Dark grey phase	Cubic	Face centered	6.68

[0014] Energy Dispersive Spectrometer (EDS) composition analysis has shown that the chemical composition of the two phases are different. The dark grey phase presents higher Ni content than the light grey phase, whereas the light grey phase presents lower content of Si, Mn and Cr than the darker phase. The Fe amount is about the same in both phases.

[0015] The two phases present in this high entropy alloy as cast, generate sever distortions in the crystalline network, which advantageously result in an increase in wear resistance compared with single phase alloys.

[0016] For example, Figure 1 shows the scanning electron microscope (SEM) image of a particular high entropy alloy as cast of the invention, herein referred to as alloy VI as cast, in which about 50% of each phase coexists; after heat treatment, as shown in Figure 2, the amount of dark grey phase has increased its proportion to around 75 %.

[0017] Figure 3 and Figure 4 show each the result of the chemical composition of each of the two phases shown in Figure 1 and Figure 2, as determined by EDS composition analysis: the light grey phase has a composition as seen in Figure 4, with higher nickel content and lower content of Si, Mn and Cr than the dark grey phase; and the dark grey phase has a composition as seen in Figure 3. The Fe amount is about the same in both phases.

[0018] The hardness of the high entropy alloy as cast of the invention surprisingly increases exponentially with an increasing content of Si in the alloy composition. In this sense the hardness of the high entropy alloy of the invention can be tuned according to the need in each particular case.

[0019] Figure 5 is a graphic showing the hardness evolution of the following exemplary high entropy alloys of the invention, as cast (discontinuous line) and after heat treatment (continuous line), which chemical compositions are the following:

Table 1

Alloy composition	**Si (wt. %)**	**Mn (wt. %)**	**Cr (wt. %)**	**Ni (wt. %)**	**Fe (wt. %)**	**Hardeness As cast HV**	**Hardeness Heat treated HV**
I	**0.34**	**19.2**	**17.9**	**62.3***	**0.26**	**159**	**175**

(continued)

Alloy composition	Si (wt. %)	Mn (wt. %)	Cr (wt. %)	Ni (wt. %)	Fe (wt. %)	Hardeness As cast HV	Hardeness Heat treated HV
II	**4.33**	**19.5**	**11.2**	**64.1***	**0.87**	**313**	**345**
III	**5.7**	**19.9**	**9.06**	**64.4***	**0.94**	**371**	**427**
IV	**6.33**	**18.4**	**10.3**	**59.2***	**5.77**	**310**	**393**
V	**8.83**	**19.4**	**10.6**	**59.2***	**1.97**	**581**	**581**
VI	**12**	**23.2**	**10.6**	**53.2***	**1.00**	**720**	**1009**
* This wt. % includes unavoidable impurities.							

[0020] The graphic shows how the hardness of the high entropy alloys as cast of the invention increases with increasing amount of Si in the composition. In their corresponding SEM images, as that of Figure 1, this increase in hardness with increasing amount of Si is reflected by an increase in the corresponding dark grey phase of each of the alloys. Accordingly in some examples the Si amount in the high entropy alloy as cast composition is comprised between 4 and 20 wt. %, preferably between 6 and 20 wt. %, more preferably between 8 and 20 wt. %, even more preferably between 10 and 20wt. % or between 12 and 20wt. %, still more preferably between 14 and 20wt. % or between 16 and 20wt. %, or between 18 and 20 wt. %.

[0021] In some other examples of the alloy the Si amount is between 4 and 16 wt. %, or for example between 6 and 14wt. %, or preferably between 8 and 13wt. %, or between 9 and 12 wt. %.

[0022] The present disclosure also provides a further high entropy alloy, referred herein to as the heat-treated high entropy alloy of the invention which consists of the following same chemical composition as the alloy as cast.

Cr:	5.0 - 20 wt. %
Mn:	10.0- 25 wt. %
Si:	0.3 - 20 wt. %
Fe:	0.2 - 6 wt. %

the balance being Ni and unavoidable impurities
which presents higher hardness than the corresponding high entropy alloy as cast.

[0023] In some examples of the high entropy alloys as cast and heat treated, the Cr amount is comprised between 8 to 19wt. %, or for example between 9 and 15wt. %, preferably between 10 and 11wt. %.

[0024] In some other examples of the high entropy alloys the Mn amount is comprised between 13 to 22wt. %, or for example between 15 and 20wt. %. In some preferred embodiments the Mn amount is between 19 and 24wt. %.

[0025] In some further examples of the high entropy alloys the Ni amount is comprised between 45 and 70wt. %, or for example between 50 and 67wt. %, preferably between 53 and 65wt. %.

[0026] In still further examples of the high entropy alloys the Fe is amount is comprised between 0.2 and 2wt. % or between 2.5 and 4wt. %, or between 4.5 and 5.8wt. %.

[0027] The skilled person understands that all the above disclosed ranges and subranges of each Cr, Mn, Si, Fe and Ni can be combined and that the resulting combinations are intended to be included in the scope of the present invention both for the as cast and heat-treated high entropy alloys.

[0028] Thus, for example some high entropy alloys consist of 4 to 20wt. % of Si, 8 to 19wt. % or 9 to 15wt. % or 10 to 11wt. % of Cr, 13wt. % to 22wt. % of Mn, 0.2 to 6wt. % of Fe, the rest being Ni and unavoidable impurities.

[0029] In some other examples the high entropy alloys consist of 4 to 20wt. % of Si, 8 to 19wt. % or 9 to 15wt. % or 10 to 11wt. % of Cr, 15 to 20wt. % of Mn, 0.2 to 6wt. % of Fe the rest being Ni and unavoidable impurities.

[0030] In some other examples the high entropy alloys consist of 4 to 20wt. % of Si, 8 to 19wt. % or 9 to 15wt. % or 10 to 11wt. % of Cr, 19 to 24wt. % of Mn, 0.2 to 6wt. % of Fe the rest being Ni and unavoidable impurities.

[0031] In some other examples the high entropy alloys consist of 6 to 20wt. %, or 8 to 20wt. %, or 10 to 20wt. %, or 14 to 20wt. %, or 16 to 20wt. %, or 18 to 20wt. % of Si, 10wt. % to 11wt. % of Cr, 19wt. % to 24wt. % of Mn, 0.2 to 6wt. % of Fe the rest being Ni and unavoidable impurities.

[0032] In some other examples the high entropy alloys consist of 6 to 20wt. %, or 8 to 20wt. %, or 10 to 20wt. %, or 14 to 20wt. %, or 16 to 20wt. %, or 18 to 20wt. % of Si, 10wt. % to 11wt. % of Cr, 13wt. % to 22wt. % of Mn, 0.2 to 6wt. % of Fe, the rest being Ni and unavoidable impurities.

[0033] In some other examples the high entropy alloys consist of 6 to 20wt. %, or 8 to 20wt. %, or 10 to 20wt. %, or

14 to 20wt. %, or 16 to 20wt. %, or 18 to 20wt. % of Si, 10wt. % to 11wt. % of Cr, 15wt. % to 20wt. % of Mn, 0.2 to 6wt. % of Fe, the rest being Ni and unavoidable impurities.

[0034] In some other examples the high entropy alloys consist of 6 to 20wt. %, or 8 to 20wt. %, or 10 to 20wt. %, or 14 to 20wt. %, or 16 to 20wt. %, or 18 to 20wt. % of Si, 9wt. % to 15wt. % of Cr, 19wt. % to 24wt. % of Mn, 0.2 to 6wt. % of Fe, the rest being Ni and unavoidable impurities.

[0035] In some other examples the high entropy alloys consist of 6 to 20wt. %, or 8 to 20wt. %, or 10 to 20wt. %, or 14 to 20wt. %, or 16 to 20wt. %, or 18 to 20wt. % of Si, 9wt. % to 15wt. % of Cr, 13wt. % to 22wt. % of Mn, 0.2 to 6wt. % of Fe, the rest being Ni and unavoidable impurities.

[0036] In some other examples the high entropy alloys consist of 6 to 20wt. %, or 8 to 20wt. %, or 10 to 20wt. %, or 14 to 20wt. %, or 16 to 20wt. %, or 18 to 20wt. % of Si, 9wt. % to 15wt. % of Cr, 15wt. % to 20wt. % of Mn, 0.2 to 6wt. % of Fe, the rest being Ni and unavoidable impurities.

[0037] In some other examples the high entropy alloys consist of 6 to 20wt. %, or 8 to 20wt. %, or 10 to 20wt. %, or 14 to 20wt. %, or 16 to 20wt. %, or 18 to 20wt. % of Si, 8 to 19wt. % of Cr, 19wt. % to 24wt. % of Mn, 0.2 to 6wt. % of Fe, the rest being Ni and unavoidable impurities.

[0038] In some other examples the high entropy alloys consist of 6 to 20wt. %, or 8 to 20wt. %, or 10 to 20wt. %, or 14 to 20wt. %, or 16 to 20wt. %, or 18 to 20wt. % of Si, 8 to 19wt. % of Cr, 13wt. % to 22wt. % of Mn, 0.2 to 6wt. % of Fe, the rest being Ni and unavoidable impurities.

[0039] In some other examples the high entropy alloys consist of 6 to 20wt. %, or 8 to 20wt. %, or 10 to 20wt. %, or 14 to 20wt. %, or 16 to 20wt. %, or 18 to 20wt. % of Si, 8 to 19wt. % of Cr, 15wt. % to 20wt. % of Mn, 0.2 to 6wt. % of Fe, the rest being Ni and unavoidable impurities.

[0040] In some other examples the high entropy alloys consist of 4 to 16wt. %, or 6 to 14wt. %, or 8 to 13wt. % of Si, 9wt. % to 15wt. % of Cr, 19wt. % to 24wt. % of Mn, 0.2 to 6wt. % of Fe, the rest being Ni and unavoidable impurities.

[0041] In some other examples the high entropy alloys consist of 4 to 16wt. %, or 6 to 14wt. %, or 8 to 13wt. % of Si, 9wt. % to 15wt. % of Cr, 13wt. % to 22wt. % of Mn, 0.2 to 6wt. % of Fe, the rest being Ni and unavoidable impurities.

[0042] In some other examples the high entropy alloys consist of 4 to 16wt. %, or 6 to 14wt. %, or 8 to 13wt. % of Si, 9wt. % to 15wt. % of Cr, 15wt. % to 20wt. % of Mn, 0.2 to 6wt. % of Fe, the rest being Ni and unavoidable impurities.

[0043] In some other examples the high entropy alloys consist of 4 to 16wt. %, or 6 to 14wt. %, or 8 to 13wt. % of Si, 8 to 19wt. % of Cr, 19wt. % to 24wt. % of Mn, 0.2 to 6wt. % of Fe, the rest being Ni and unavoidable impurities.

[0044] In some other examples the high entropy alloys consist of 4 to 16wt. %, or 6 to 14wt. %, or 8 to 13wt. % of Si, 8 to 19wt. % of Cr, 13wt. % to 22wt. % of Mn, 0.2 to 6wt. % of Fe, the rest being Ni and unavoidable impurities.

[0045] In some other examples the high entropy alloys consist of 4 to 16wt. %, or 6 to 14wt. %, or 8 to 13wt. % of Si, 8 to 19wt. % of Cr, 15wt. % to 20wt. % of Mn, 0.2 to 6wt. % of Fe, the rest being Ni and unavoidable impurities.

[0046] In some other examples the high entropy alloys consist of 4 to 16wt. %, or 6 to 14wt. %, or 8 to 13wt. % of Si, 10wt. % to 11wt. % of Cr, 19wt. % to 24wt. % of Mn, 0.2 to 6wt. % of Fe, the rest being Ni and unavoidable impurities.

[0047] In some other examples the high entropy alloys consist of 4 to 16wt. %, or 6 to 14wt. %, or 8 to 13wt. % of Si, 10wt. % to 11wt. % of Cr, 13wt. % to 22wt. % of Mn, 0.2 to 6wt. % of Fe, the rest being Ni and unavoidable impurities.

[0048] In some other examples the high entropy alloys consist of 4 to 16wt. %, or 6 to 14wt. %, or 8 to 13wt. % of Si, 10wt. % to 11wt. % of Cr, 15wt. % to 20wt. % of Mn, 0.2 to 6wt. % of Fe, the rest being Ni and unavoidable impurities.

[0049] In some other examples the high entropy alloys consist of 8 to 13wt. % of Si, 9 to 15wt. % of Cr, 15wt. % to 20wt. % of Mn, 0.2 to 6wt. % of Fe, 53wt. % to 65wt. % of Ni, and unavoidable impurities.

[0050] In some other examples the high entropy alloys consist of 8 to 13wt. % of Si, 9 to 15wt. % of Cr, 19wt. % to 24wt. % of Mn, 0.2 to 6wt. % of Fe, 53wt. % to 65wt. % of Ni, and unavoidable impurities.

[0051] In some other examples the high entropy alloys present 8 to 13wt. % of Si, 10 to 11wt. % of Cr, 13wt. % to 22wt. % of Mn, 0.2 to 6wt. % of Fe, 53wt. % to 65wt. % of Ni, and unavoidable impurities.

[0052] In some other examples the high entropy alloys consist of 6 to 14wt. % of Si, 8 to 19wt. % of Cr, 15wt. % to 20wt. % of Mn, 0.2 to 6wt. % of Fe, 53wt. % to 65wt. % of Ni, and unavoidable impurities.

[0053] In some other examples the high entropy alloys consist of 6 to 14wt. % of Si, 9 to 15wt. % of Cr, 19wt. % to 24wt. % of Mn, 0.2 to 6wt. % of Fe, 53wt. % to 65wt. % of Ni, and unavoidable impurities.

[0054] In some other examples the high entropy alloys present 6 to 14wt. % of Si, 10 to 11wt. % of Cr, 15wt. % to 20wt. % of Mn, 0.2 to 6wt. % of Fe, 53wt. % to 65wt. % of Ni, and unavoidable impurities.

[0055] In some examples the high entropy alloys consist of 4 to 13wt. % of Si, 9 to 19wt. % of Cr, 18 to 24wt. % of Mn, 0.2 to 6wt. % of Fe, and 53wt. % to 65wt. % of Ni with unavoidable impurities.

[0056] In some preferred examples the high entropy alloys consist of 4 to 12wt. % of Si, 9wt. % to 12wt. % of Cr, 18wt. % to 24wt. % of Mn, 0.5 to 6wt. % of Fe, and 53wt. % to 65wt. % of Ni with unavoidable impurities.

[0057] In some also preferred examples the high entropy alloys consist of 8 to 12.5wt. % of Si, 10wt. % to 11wt. % of Cr, 19wt. % to 24wt. % of Mn, 1.0 to 2.0wt. % of Fe, and 53wt. % to 60wt. % of Ni with unavoidable impurities.

[0058] Also preferred examples of the high entropy alloys consist of one composition selected from the following compositions, and in particular alloy VI and alloy V

Alloy composition	Si (wt. %)	Mn (wt. %)	Cr (wt. %)	Ni (wt. %)	Fe (wt. %)
I	0.34	19.2	17.9	62.3*	0.26
II	4.33	19.5	11.2	64.1*	0.87
III	5.7	19.9	9.06	64.4*	0.94
IV	6.33	18.4	10.3	59.2*	5.77
V	8.83	19.4	10.6	59.2*	1.97
VI	12	23.2	10.6	53.2*	1.00
* This wt. % includes unavoidable impurities.					

[0059] The inventors have found that the high entropy alloy as cast of the invention can be submitted to a hardening heat treatment rendering a modified high entropy alloy, herein referred to as the heat-treated high entropy alloy, which presents higher hardness compared to the corresponding high entropy alloy as cast. The higher is the Si content, the higher is the increment in hardness. The dark/light phase ratio also increases. The increment of dark phase is evident in Figure 2.

[0060] It has also been seen that the presence of a Si amount preferably equal or greater than 4wt. % and up to 20wt. % enhances during heat treatment the promotion of the formation of dark grey phase that results in a hardening of the heat-treated high entropy alloy. An example is shown in Figure 2.

[0061] In some examples the Si amount in the heat treated high entropy alloy composition is comprised between 4 and 20wt. %, preferably between 6 and 20wt. %, more preferably between 8 and 20wt. %, even more preferably between 10 and 20wt. % or between 12 and 20wt. %, still more preferably between 14 and 20wt. % or between 16 and 20wt. %, or between 18 and 20wt. %.

[0062] In some other examples of the heat-treated alloy the Si amount is between 4 and 16wt. %, or for example between 6 and 14wt. %, or preferably between 8 and 13wt. %, or between 9 and 12wt. %.

[0063] Figure 4 shows the hardness evolution of the exemplary heat treated high entropy alloys of the invention (continuous line) which chemical compositions are shown in Table 1 above.

[0064] The graphic shows how the hardness of the heat-treated high entropy alloys is higher than the hardness of the corresponding high entropy alloys as cast of the same composition. Further, the graphic shows how the hardness of the heat-treated high entropy alloys of the invention increases with increasing amounts of Si in their composition. The comparison of the SEM images of the alloys as cast and the corresponding heat-treated alloys of same composition show an increase in the dark grey phase which is responsible for the hardness increment. Figures 1 and 2 show the increased amount in dark grey phase for the particular case of alloy VI. The hardness was measured according the standard: UNE EN ISO 6507-1:2015 as explained under section Examples.

[0065] The increase in hardness in the alloys of the invention with an increasing amount of Si, has been observed to affect whole parts as cast and parts after their heat treatment, as a whole, that is in all their sections, as shown by the tests carried on the surface and in the nucleus of the 30 x 30 x 10 mm test samples, at 1-2 mm from the surface and at 27-28 mm towards the inside of the test sample, respectively.

[0066] Contrary to the case of the present high entropy alloys, conventional alloys such as tool steel, white cast iron, and manganese steels are either softened during heat treatment or suffer severe cracks when the cooling speed for hardening is increased to avoid perlite generation, as previously mentioned in the Background of the invention.

[0067] Whereas white cast iron, manganese steels and tools steels show Vickers hardness typically within the range of about 240 to about 640 HV, the high entropy alloys as cast of the invention show higher hardness values which are in general equal or greater than 650 HV, preferably equal or greater than 670 HV, more preferably equal or greater than 690 HV, still more preferably equal or greater than 710 HV and most preferably equal or greater than 715 HV. The heat treated alloys of the invention show even higher hardness values, which are equal or greater than 730 HV, preferably equal or greater than 775 HV, more preferably equal or greater than 850 HV, still more preferably equal or greater than 900 HV, still more preferably equal or greater than 950 HV, even more preferably equal or greater than 1000 HV, and most preferably equal or greater than 1035 HV.

[0068] In some embodiments the hardness of the alloy as cast is typically between 650 HV and less than 730 HV, for example between 670 and 710 HV, or for example between 690 and 723 HV.

[0069] In some other embodiments the hardness of the heat-treated alloy is typically between 730 and 1050 HV, for example between 775 and 1035 HV. In other embodiments the hardness of the heat-treated alloy is between 850 and 950 HV, or between 900 and 1000 HV.

[0070] In an additional aspect the invention provides a process for the preparation of the high entropy alloy as cast of the invention which comprises the following steps:

(i) Introducing in a furnace the pure elements of the alloy to be prepared,
(ii) Adding a deoxidizing product for oxygen removal,
(iii) Removing slag,
(iv) Maintaining molten state for homogenization
(v) Transferring the molten metal to a pouring ladle, and
(vi) Pouring the molten metal in a mould.

[0071] The furnace according to a particular embodiment is a conventional furnace like an induction melting furnace. The alloying elements Ni, Cr, Mn, Fe and Si are added to the furnace in step (i) in the following forms:

- Pure silica (99-100wt. % Si)
- Pure manganese (99-100wt. % Mn)
- Pure chrome (99-100wt. % Cr),
- Pure nickel (99-100wt. % Ni)
- Pure iron (99-100wt. % Fe)

[0072] in order to obtain the desired composition of the alloy of the invention. The adjustment of the additions and the desired composition can be readily carried out by a skilled person in the art.

[0073] During the process of the invention it is necessary to protect the surface of the melt in the furnace with a protective product (slag coagulation flux) to prevent oxidation losses of alloying elements and gas pick-up from the atmosphere. Further, during the process the metal can be covered with a ceramic fibre blanket in order to prevent that hydrogen from the atmosphere dissolves in the molten metal and that also metal oxidations take place.

[0074] Once the metal is molten reaction products (slag) are removed from the top of the surface in the furnace. A slag coagulation flux can be added to ease its removal with a steel stick. The furnace must be switched off to stop turbulence and allow slag floating in induction furnaces.

[0075] During the melting process oxygen and hydrogen dissolve in the melt due to generated turbulence, which can cause porosity and inclusions. If gases are not removed, they accumulate, and holes appear in the last solidification step.

[0076] Removal of oxygen is made by adding a deoxidizing product like magnesium. The deoxidizing product is in general introduced in a fixed proportion (e.g. 0.10wt. % by weight in respect of the total weight of molten metal) in the furnace once all the elements have been loaded and are molten. Hydrogen is removed by nitrogen or argon bubbling from the bottom of the furnace by means of a porous plug.

[0077] Thereafter, a further step for removing slag from the top of the surface in the furnace is carried out by switching it off and leaving the slag floating. Then it is necessary to add slag coagulation flux until slag is thick enough and is removed with the metal stick. Before pouring the melt into the mould the metal must remain molten for a period to allow a correct homogenization of the elements. Typically, time is not less than 10 minutes. The melt is transferred to a pouring ladle and poured in a mould.

[0078] The melting and pouring temperature are variable depending for example on the thickness of the part to be cast. Usually temperature is in the range of 1300°C-1500°C, for example 1500°C for parts of less than 38 mm thick, and for parts of more than 38 mm thick, 1300°C.

[0079] The invention in a further aspect relates to a process for manufacturing of the heat-treated high entropy alloy of the invention, which comprises submitting the high entropy alloy as cast of the invention to a heat treatment process.

[0080] This heat treatment process can be carried out in any conventional manner known to the skilled person in the art and comprises the steps of: submitting the high entropy alloy as cast of the invention to a high temperature and subsequent cooling. In a particular embodiment, heat treatment is done in a furnace, such as an electrical resistance non-controlled atmosphere heat treatment furnace. By way of example only, heat treatment can be carried out at temperatures between 400-1250°C. The time the alloy as cast is submitted to heat treatment varies depending on factors like the size of the part, the selected temperature, and is typically from 4 to 60 hours. Cooling media can also vary depending on the cooling rate required, and are for example, cooling inside the furnace, calm air cooling, forced air cooling, cooling in oil, or cooling in water.

[0081] In some preferred embodiments the heat treatment process is carried out at temperatures between 500 and 1200 °C, more preferably between 700 and 1100 °C, even more preferably between 800 and 1000 °C, and most preferably at about 900°C. It has been shown that temperatures about 900 °C are very effective in the sense that they allow the alloys as cast to arrive to a new thermodynamic equilibrium so that the dark phase (identified in figure 1 for alloy VI with dark grey) is precipitated in higher content generating a higher distortion in the network and thus increasing the resulting hardness and wear resistance of the heat treated high entropy alloy.

[0082] In still another aspect the invention relates to the use of the as cast and the heat-treated high entropy alloys of the invention for manufacturing parts for use in diverse sectors like machinery for construction, machine tool, hand tool, aeronautic, marine sector, energy generation, oil & gas, and mining. According to some embodiments the heat-treated high entropy alloys of the invention are preferably used for their manufacturing.

[0083] Illustrative, but non-limiting examples of parts of the as cast high entropy alloy or heat-treated high entropy alloy, preferably of the heat-treated high entropy alloy are cutting tools, grinding balls, wear covers, turbine blades, high wear and corrosion resistant valves and pipes, propellers, and movement elements of shot blasting and mining equipment.

[0084] The following examples are merely illustrative and should not be considered as limiting the invention.

EXAMPLES

[0085] For the tests carried out in relation to the present invention keel blocks Y2 were prepared using chemically bonded sand moulds, following the standard norm UNE-EN 1563:1998. Keel blocks Y2 were then extracted from the moulds and cleaned by shot blasting.

[0086] Keel blocks were then cut and test samples for micrographic inspection of rectangular dimensions of approximately 30 x 30 x 10 mm were prepared by surface polishing and their microstructures were then analysed with a field emission gun scanning electron microscope (SEM) (Model ULTRA PLUS, Zeiss).

[0087] Vickers hardness was determined using test samples of rectangular dimensions of approximately 30 x 30 x 10 mm using an INSTROM WOLPER equipment model TESTOR 971/3000. Hardness was determined in the surface and in the nucleus of the test samples: at 1-2 mm from the surface and at 27-28 mm towards the inside of the test sample, respectively.

[0088] EDS: Energy Dispersive Spectrometer (Spectrolab M10 from the company SPECTRO) was used for quantitative chemical analysis of the alloys.

[0089] Diffraction X- Ray (DRX) using a diffractometer PANalytical Xpert, equipped with a goniometric vertical copper tube (Bragg-Brentano geometry). The measuring conditions have been:

- Current type: 40 KV y 40 mA.
- Angular sweep: 5-90°2θ

Example 1: Preparation of high entropy alloys of the invention

Example 1. Alloy VI

[0090] Different pure elements selected to achieve the chemical composition shown below in Table 2 were introduced in adequate amounts an induction furnace of 50 kg of capacity. To ease the dissolution and adjustment of different alloys, certified alloys of purity higher than 99.0wt. % were used.

[0091] Melting was done until a temperature of 1490°C was achieved. Nitrogen purging was performed by the bottom of the furnace to eliminate hydrogen with a porous plug. Once the metal was molten and the slag was removed from the top of the furnace, 10 minutes were waited for adequate mixing up of the elements. The metal was transferred to a ladle. Pouring was performed into two keel blocks Y2 in order to obtain test specimens for later on testing.

[0092] The composition of the alloy VI as cast obtained can be seen in Table 2

Table 2 Chemical composition of alloy VI (wt. %)

	Ni	Cr	Mn	Si	Fe
Composition	53.2 wt. % *	10.6 wt. %	23.2 wt. %	12.0 wt. %	1wt. %
• * This wt.% includes unavoidable impurities.					

Example 2: Alloy V

[0093] Different pure elements selected to achieve the chemical composition shown below in Table 3 were introduced in adequate amounts were introduced in an induction furnace of 50 kg of capacity. To ease the dissolution and adjustment of different alloys, certified alloys of purity higher than 99.0 wt. % were used.

[0094] Melting was done until a temperature of 1486°C was achieved. Nitrogen purging was performed by the bottom of the furnace to eliminate hydrogen with a porous plug. Once the metal was molten and the slag was removed from the top of the furnace, 10 minutes were waited for adequate mixing up of the elements. The metal was transferred to a ladle. Pouring was performed into two keel blocks Y2 in order to obtain test specimens for later on testing.

[0095] The final composition of the alloy V as cast obtained can be seen in Table 3

Table 3 Chemical composition of alloy V (wt. %)

	Ni	Cr	Mn	Si	Fe
Composition	59.2 wt. % *	10.6 wt. %	19.4 wt. %	8.83wt. %	1.97wt. %
• * This wt. % includes unavoidable impurities.					

Example 3: Microstructure analysis

[0096] SEM (Scanning Electron Microscopy) was used to identify existing phases in samples extracted from alloy V as cast and after heat treatment.

[0097] The SEM images are shown in Figure 1 and 2 where the two different phases are seen and marked with clear grey and a dark grey colour. The two detected phases show different morphology and different chemical compositions.

[0098] EDS (Energy Dispersive Spectrometer) was used for the chemical analysis of the elements present in the two phases and resulted in the compositions shown in Figure 3 (dark grey phase) and Figure 4 (light grey phase).

[0099] It has been determined that the phases are similar to those appearing in nickel base superalloys.

Example 4: Hardness and heat treatment process

[0100] The VI alloy as cast obtained in Example 1 was heat treated and hardness tests were performed before and thereafter.

[0101] Two types of heat treatments were performed to two separate samples of the VI alloy as cast comprising:

(i) heating up to 900°C for two hours and cooling in water, or
(ii) heating up to 900°C for two hours and calm air cooling

[0102] Hardness was determined in the surface and in the nucleus of the as cast alloy and the heat treated alloy by using the 30 x 30 x 10 mm test samples described before and analysing the hardness at 1-2 mm from the surface and at 27-28 mm towards the inside of the test samples.

[0103] After both heat treatments a remarkable increase of hardness has been seen both in the nucleus and in the surface of the alloys. In the nucleus hardness increased up to 1025 HV after the heat treatment (i), and up to 1035 HV after the heat treatment (ii). The results are shown in following Table 4:

Table 4.-Hardness comparison for alloy VI

	HV		
	As Cast	(i) heat treated 900°C 2 hours and water cooling	(ii) heat treated 900°C 2 hours and calm air cooling
VI Surface	723	992	983
VI Nucleus	718	1025	1035

Example 5 Corrosion resistance

[0104] In this example the corrosion behaviour of commercial alloy AISI 347, which is one of the most representative corrosion resistant alloys, was compared with that of alloy VI and alloy V as cast manufactured according to Example 1 and Example 2 respectively and submitted to the heat treatment (ii) defined in Example 4.

[0105] The corrosion test was carried for 648 hours, using a salt spray chamber and following the standard UNE EN-ISO 9227:2007. Images of the alloys V and VI heat treated after the test can be seen in Figure 6. It can be seen that there is no corrosion in the surface of the alloys of the invention once the test has finished. Sample d) corresponds to alloy 1.2842 submitted to the corrosion test for comparison and only for 48 hours after which the sample showed corrosion.

Claims

1. A high entropy alloy as cast consisting of the following chemical composition, wherein the percentages are expressed by weight with respect to the total weight of the alloy:

Cr:	5.0 - 20wt. %
Mn:	10.0- 25wt. %
Si:	0.3 - 20wt. %
Fe:	0.2 - 6.0wt. %

the balance being Ni and unavoidable impurities

2. The alloy of claim 1, wherein the Si amount in the alloy is comprised between 4 and 20 wt.%, preferably between 6 and 20 wt.%, more preferably between 8 and 20 wt.%, even more preferably between 10 and 20 wt.% or between 12 and 20 wt.%, still more preferably between 14 and 20 wt.% or between 16 and 20wt. %, or between 18 and 20wt. %..

3. The alloy of claim 1, wherein the Si amount is between 4 and 16wt. %, or between 6 and 14wt. %, or preferably between 8 and 13wt. %, or between 9 and 12wt. %.

4. The alloy of any one of claims 1 to 3, wherein the Cr amount is comprised between 8 to 19wt. %, or between 9 and 15wt. %, preferably between 10 and 11wt. %.

5. The alloy of any one of claims 1 to 4, wherein the Mn amount is comprised between 13 to 22wt. %, or between 15 and 20wt. %, preferably between 19 and 24wt. %.

6. The alloy of any one of claims 1 to 5, wherein the Ni amount is comprised between 45 and 70wt. %, or between 50 and 67wt. %, preferably between 53 and 65wt. %.

7. The alloy of any one of claims 1 to 6 consisting of 4 to 13wt. % of Si, 9 to 19wt. % of Cr, 18 to 24wt. % of Mn, 0.2 to 6wt. % of Fe, and 38wt. % to 68wt. % of Ni with unavoidable impurities.

8. The alloys of any of claims 1 to 7 consisting of 8 to 12.5wt. % of Si, 10wt. % to 11wt. % of Cr, 19wt. % to 24wt. % of Mn, 1.0 to 2.0wt. % of Fe, and 53wt. % to 60wt. % of Ni with unavoidable impurities

9. The alloy of any one of claims 1 to 8 comprising a microstructure consisting of one first phase and a second phase, wherein the first phase of FCC (Face Center Cubic) crystals presents higher Ni content and lower content of Si, Mn and Cr than the second phase, and the second FCC phase presents lower Ni content and higher contents of Si, Mn and Cr.

10. The alloy of any one of claims 1 to 9, presenting hardness values equal or greater than 650 HV, preferably equal or greater than 670 HV, more preferably equal or greater than 690 HV, still more preferably equal or greater than 710 HV and most preferably equal or greater than 715 HV.

11. A process for the preparation of the high entropy alloy as cast according to any one of previous claims which comprises the following steps:

(i) Introducing in a furnace the pure elements of the alloy to be prepared,
(ii) Adding a deoxidizing product for oxygen removal,
(iii) Removing slag,
(iv) Maintaining metal in molten condition for homogenization
(v) Adjusting the chemical composition.
(vi) Transferring the molten metal to a pouring ladle, and
(vii) Pouring the molten metal in a mould.

12. A process for the preparation of a heat-treated high entropy alloy which comprises a heat treatment process which comprises the steps of:

- submitting the high entropy alloy as cast according to any one of claims 1 to 10 to a heat treatment at a temperature comprised between 500 and 1200 °C, and
- subsequent cooling in calm air.

13. A heat-treated high entropy alloy consisting of the composition as defined in any one of claims 1 to 10 with a higher hardness than the corresponding high entropy alloy as cast of same chemical composition.

14. The heat-treated alloy according to claim 13, presenting hardness values equal or greater than 730 HV, preferably equal or greater than 775 HV, more preferably equal or greater than 850 HV, still more preferably equal or greater than 900 HV, still more preferably equal or greater than 950 HV, even more preferably equal or greater than 1000 HV, and most preferably equal or greater than 1035 HV.

15. An alloy according to any one of claims 1 to 10 and 13-14 consisting of a composition selected from the following compositions:

Alloy composition	Si (wt. %)	Mn (wt. %)	Cr (wt. %)	Ni (wt. %)	Fe (wt. %)
I	0.34	19.2	17.9	62.3*	0.26
II	4.33	19.5	11.2	64.1*	0.87
III	5.70	19.9	9.06	64.4*	0.94
IV	6.33	18.4	10.3	59.2*	5.77
V	8.83	19.4	10.6	59.2*	1.97
VI	12.0	23.2	10.6	53.2*	1.00
* This wt. % includes unavoidable.					

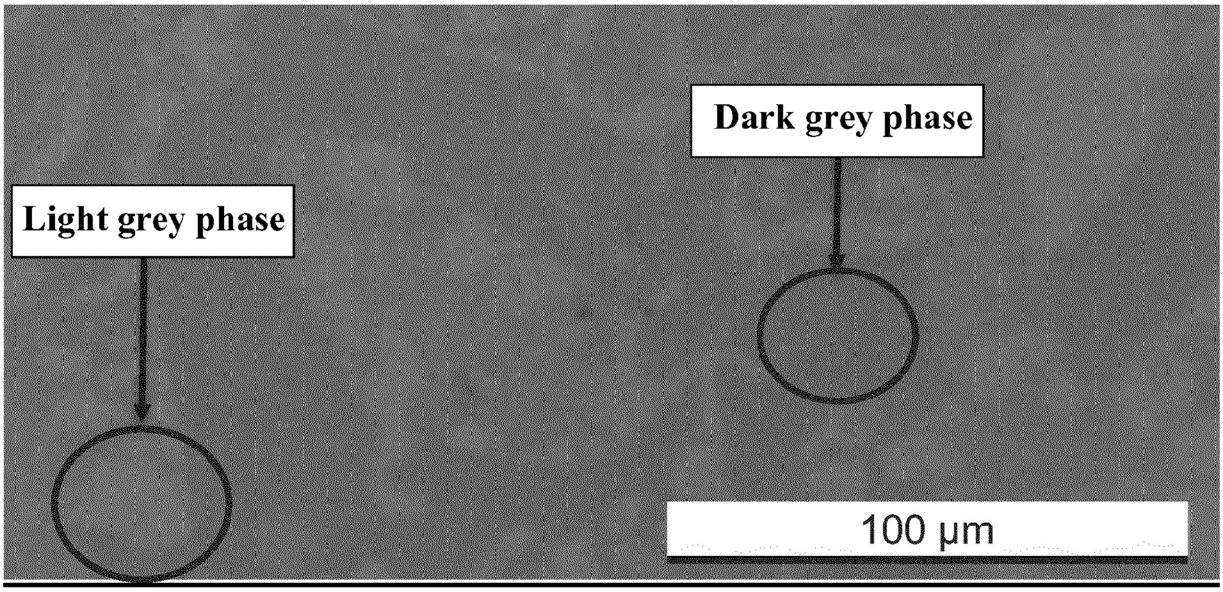

Dark grey phase
Light grey phase
100 µm

FIG. 1

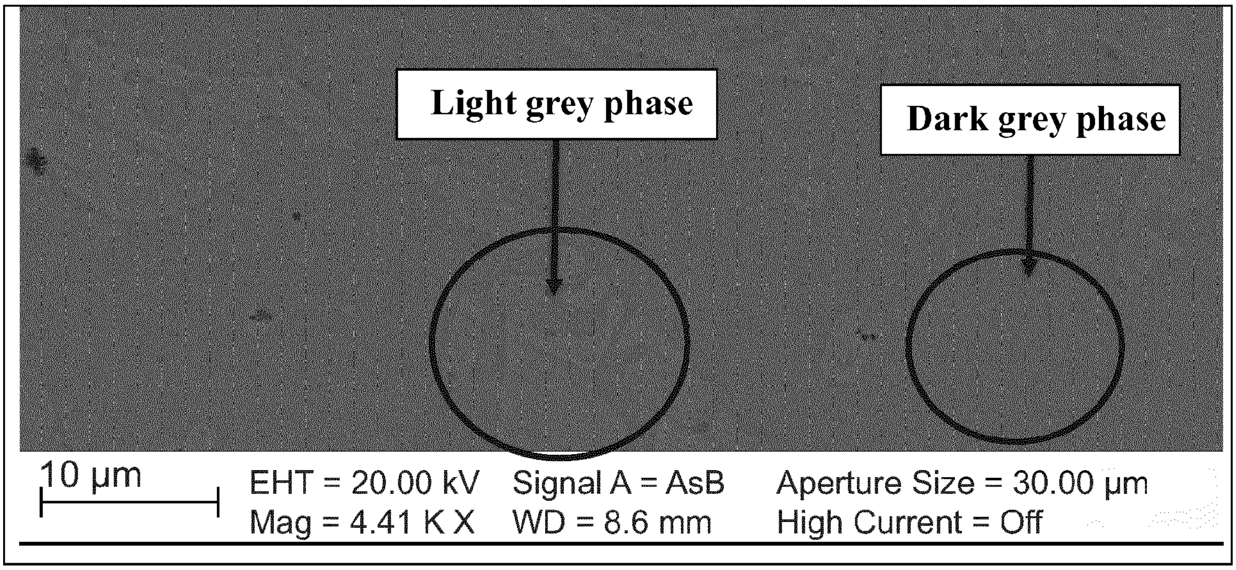
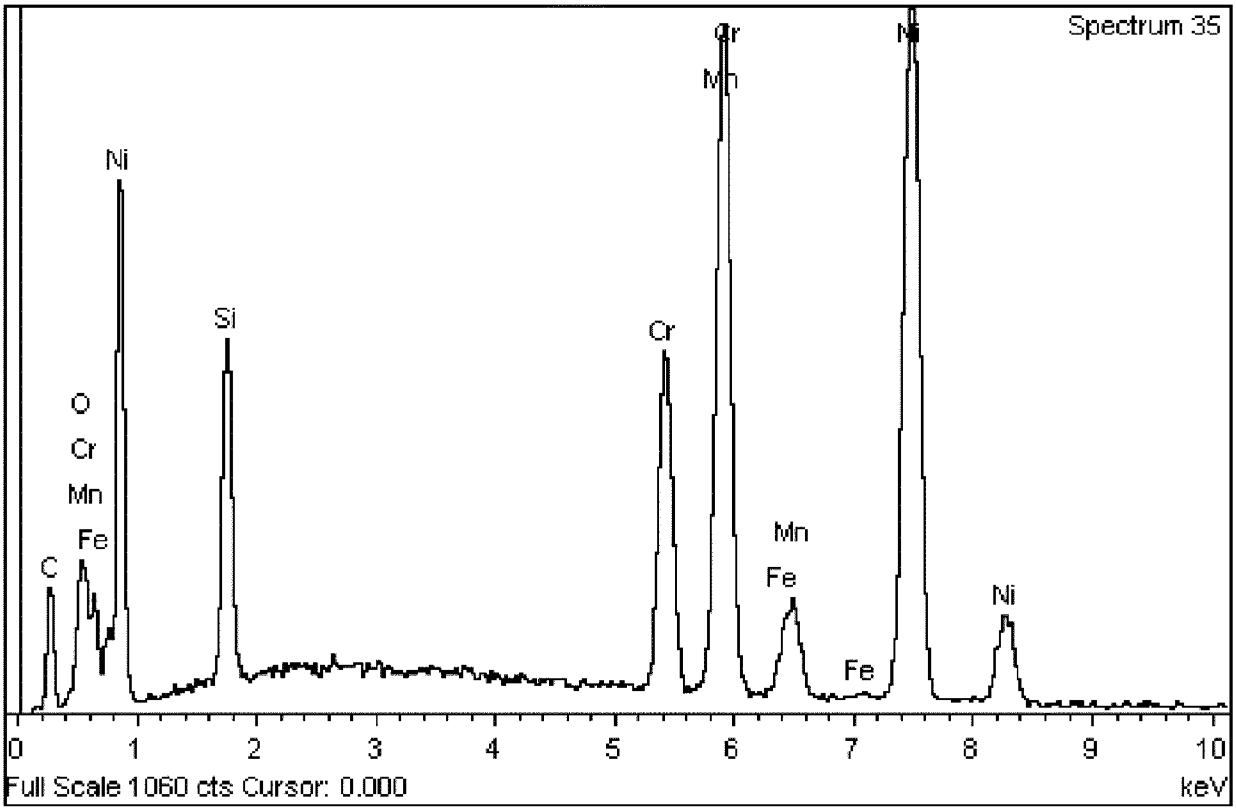

Light grey phase
Dark grey phase
10 µm
EHT = 20.00 kV
Mag = 4.41 K X
Signal A = AsB
WD = 8.6 mm
Aperture Size = 30.00 µm
High Current = Off

FIG. 2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Si
Cr
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Mn
Fe
C
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Fe
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3
4
5
6
7
8
9
10
Full Scale 1060 cts Cursor: 0.000
keV

FIG. 3

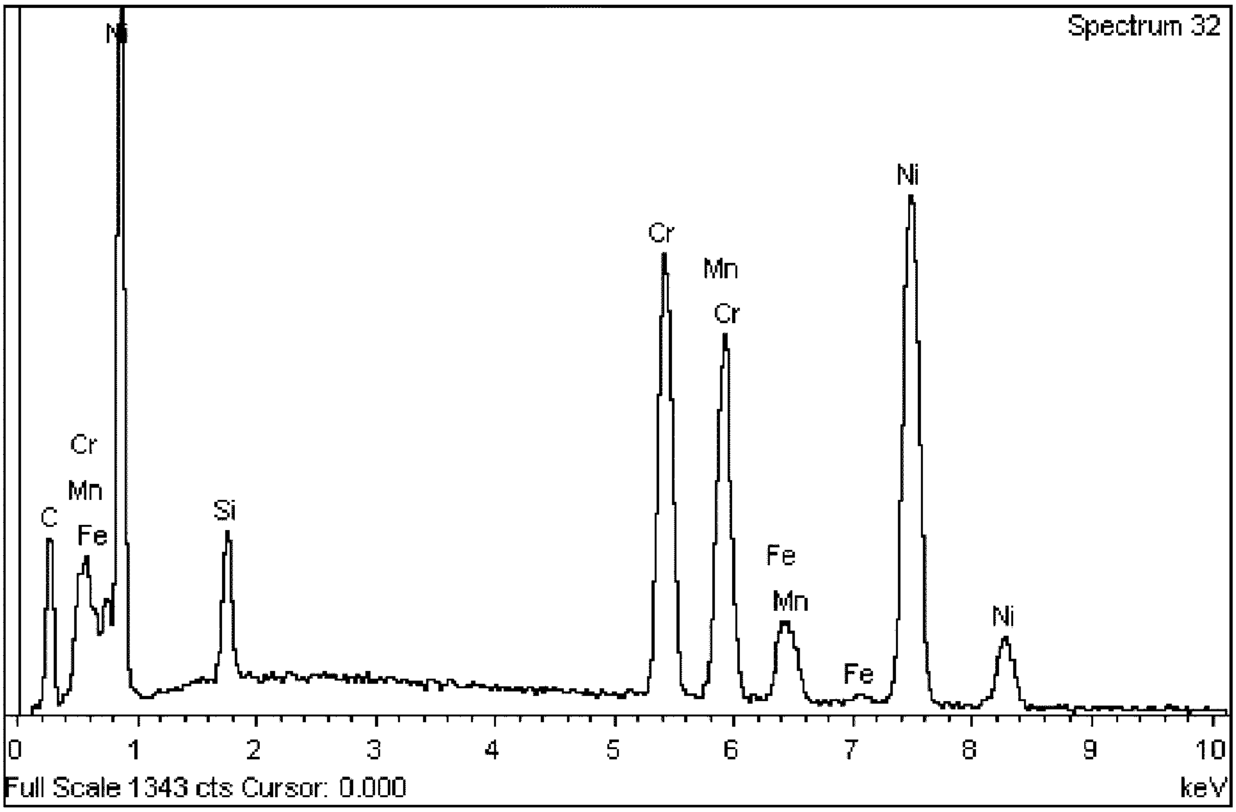
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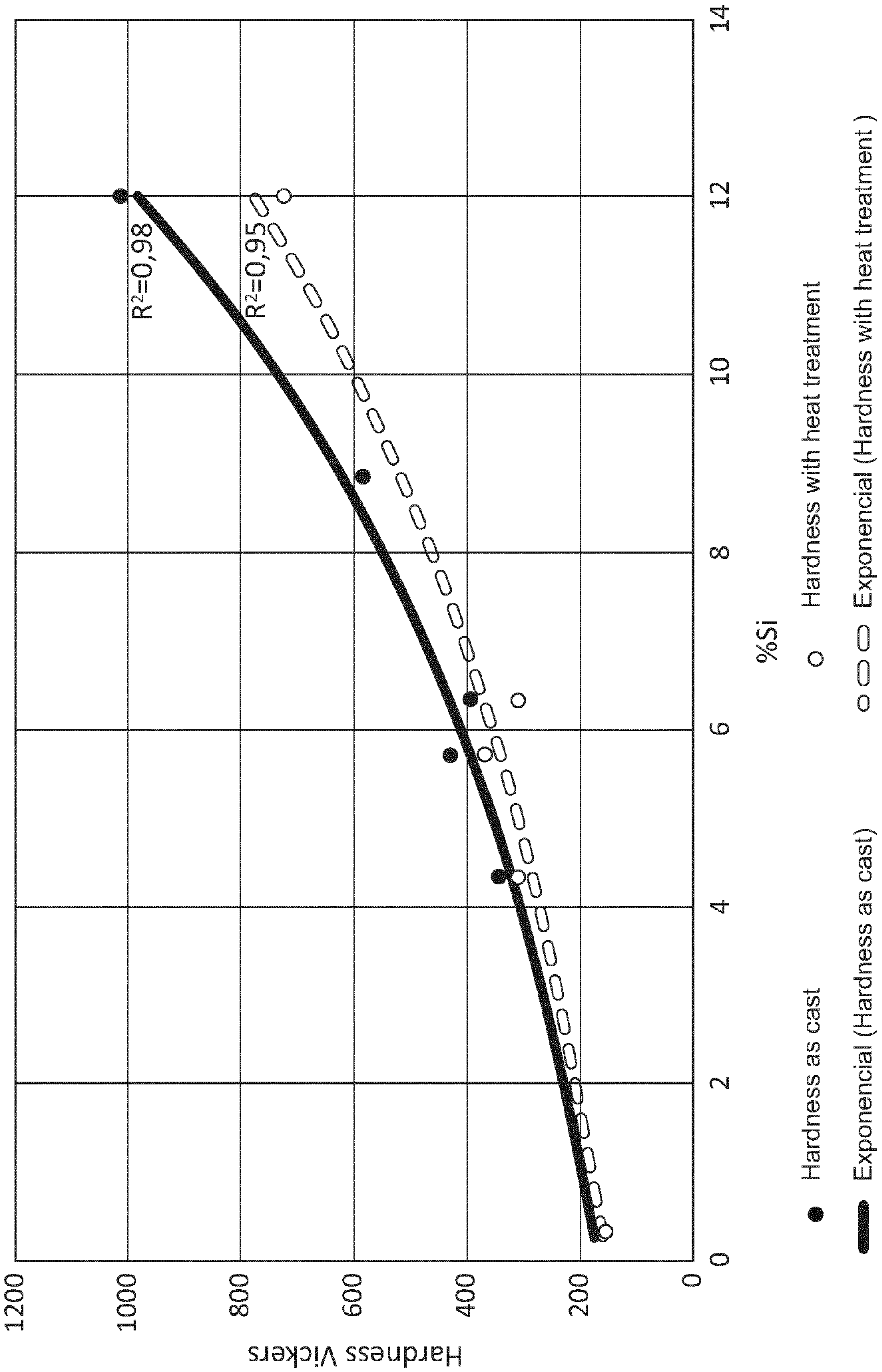
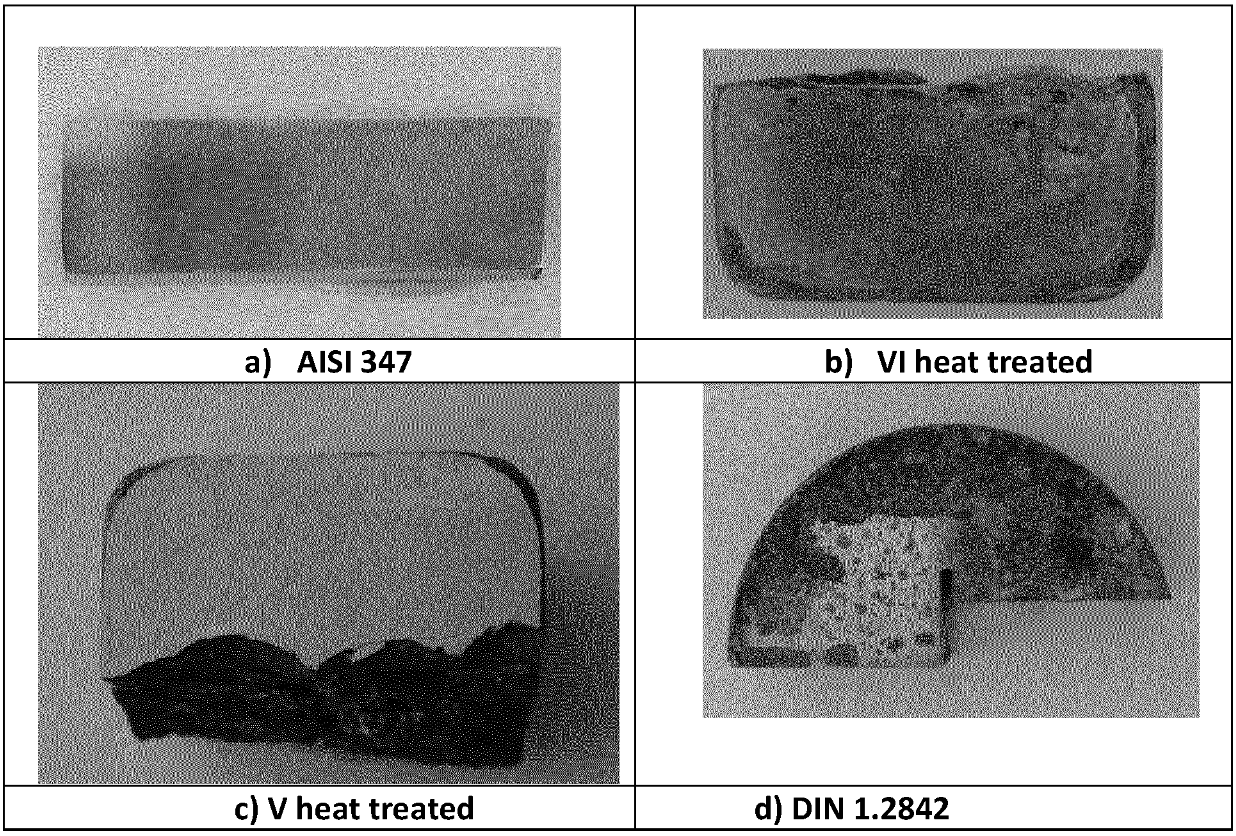
FIG. 4



Hardness Vickers
0
200
400
600
800
1000
1200
%Si
0
2
4
6
8
10
12
14
R²=0,98
R²=0,95
Hardness as cast
Exponencial (Hardness as cast)
Hardness with heat treatment
Exponencial (Hardness with heat treatment)

FIG. 5



a) AISI 347

b) VI heat treated

c) V heat treated

d) DIN 1.2842

FIG. 6

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 18 38 2941

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	CN 104 233 003 A (YANCHENG XINYANG ELECTRIC HEATING MATERIAL CO LTD) 24 December 2014 (2014-12-24) * claims 1-6; example 1 * -----	1-15	INV. C21D9/22 C21D1/18 C22C1/02 C22C1/06 C22C19/00 C22C19/05 C22F1/10
A	MICHAEL C. GAO ET AL: "High Entropy Functional Materials", JOURNAL OF MATERIALS RESEARCH, vol. 33, no. 19, 20 September 2018 (2018-09-20), pages 3138-3155, XP055545996, US ISSN: 0884-2914, DOI: 10.1557/jmr.2018.323 * page 3138 - page 3152 * -----	1-15	
			TECHNICAL FIELDS SEARCHED (IPC)
			C21D C22C C22F

The present search report has been drawn up for all claims

3

Place of search	Date of completion of the search	Examiner
The Hague	14 March 2019	Kreutzer, Ingo

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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D : document cited in the application
L : document cited for other reasons
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& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 18 38 2941

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14-03-2019

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 104233003 A	24-12-2014	NONE	

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82