



High Entropy Cantor Alloys (HEAs) modification induced by tungsten alligation, heat treatment and deep cold plastic deformation

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ABSTRACT. High Entropy Alloys (HEAs) is a unique class of materials that combine particular properties in a large-scale of temperatures, able to guarantee new unexplored materials and alloys with several potentially engineering applications (i.e. space and aerospace industries). As promising structural materials, HEAs consist of five or more principal elements. As a consequence of the monophasic microstructure which usually characterizes HEAs, these alloys offer an excellent combination of strength, strain hardening ability, good plasticity, ductility and fracture toughness especially at cryogenic temperatures better than the existing conventional metals and alloys. For the above reasons, the present work deals with Classic Cantor alloy, a well-known CoCrFeMnNi HEA, where mechanical properties were improved using low cost casting techniques and a combination of different metallurgical methodologies (heat treatment, cold working and adding alloying elements). A promising alloy element, tungsten, was used in the experimentation where mechanical and microstructural characterization was performed using different techniques.

KEYWORDS. High Entropy Alloys (HEAs), Cantor Alloy, Tungsten (W) alligation, Mechanical characterization; Heat treatments, Microstructure characterization.



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INTRODUCTION

High Entropy Alloys (HEAs) represent a unique class of materials that combine particular properties in a large-scale of temperatures, able to guarantee new unexplored materials and alloys with several potentially engineering applications (i.e. space and aerospace industries) [1-3]. As promising structural materials, HEAs consist of five or more principal elements whose concentrations vary from 5 to 35 in equal or near equal atomic percent (%_{at}) [2, 4]. The main principle which drives the choice of the main elements of the alloy is to increase mixing entropy, reduce the Gibbs free energy and inhibit the generation of intermetallic compounds [5]. Many parameters influence the microstructure and the properties of the alloy: enthalpy and entropy of mixing, atomic size difference, average melting point, electron concentration expressed as electron per atom ratio (e/a) and valence electron concentration (VEC). The combination of these parameters highly influences possible obtainable microstructure (disordered or ordered solid solution, mono or polyphasic microstructures...) and then the properties of the material.

HEAs offer an excellent combination of strength, strain hardening ability, good plasticity, ductility and fracture toughness especially at cryogenic temperatures better than the existing conventional metals and alloys [6]. The majority of reported HEAs compositions are based on the transition metals, namely Co, Cr, Fe and Ni, with addition of elements like Al, Cu, Mn, V, Ti, and Mo [1–13]. Several combinations of these elements can develop high entropy alloys characterized by simple monophasic structures (usually face centred cubic crystals) and very promising mechanical properties (high strength and high ductility). Researchers efforts are directed towards finding new alloy compositions, modifying those just studied, in order to develop materials with properties which can fit the requirements of the designers [7].

One of the first High Entropy Alloys to be investigated is the single-phase face-centred cubic (fcc) CoCrFeMnNi HEA, commonly known as the Cantor alloy. These five alloy elements are all transition elements with very similar physical properties (atomic radius, valence...). It is a classic example of a complex concentrated alloy characterized by high strength and high ductility, properties preserved also at cryogenic temperatures. These properties are achieved as a result of deformation mechanisms of slip and twinning allowed by the obtained ordered monophasic fcc [8-9], while the impressive cryogenic properties are usually attributed to the development of nano-twinning [10].

In order to improve the properties of HEAs, their composition has been modified with the addition of different elements in concentration lower than 5 %_{at}. Over this limit the element is considered the main element. The strengthening mechanisms are different and depend on added elements and go from the solid solution strengthening to the development of second strengthening phases after heat treatment. The presence of interstitial or substitutional atoms inside the crystallographic reticules modifies the mechanisms related to the deformation process.

The use of doping with nitrogen or carbon in HEAs matrix is a tested way in which interstitial atoms have atomic radius sensibly smaller than those of the main HEAs elements (CoCrFeMnNi). Nitrogen addition can improve the strength of a Cantor alloy without loss of ductility, and an improvement of the strength at cryogenic temperature [11]. Nitrogen seems to increase Cantor properties through both precipitation of nitride particles (Me_2N) and solid solution strengthening and lattice friction effect. Similar effect has been shown by HEAs modified with carbon addition. Carbon produces several kinds of carbides which segregate at the grain boundary retarding recrystallization. This leads to finer microstructures [12, 13].

Other recent studies are focused on the effect of alligation with elements characterized by an atomic radius higher than those of the HEAs matrix. These elements usually replace the atoms and create a substitutional solid solution. The tension induced by the presence of bigger atoms in the crystallographic reticulus produces internal elastic tensions which increase the mechanical properties of the material and/or keep it able to heat treated (precipitation hardening).

The addition of vanadium induces the precipitation of an intermetallic phase (σ phase) which increases the yield strength [14, 15]. Aluminium additions up to 8 % do not modify the properties of Cantor HEAs. Only a little reduction of the ductility is observed in the alloys that keep a FCC solid solution. Over this limit aluminium induces the formation of a duplex fcc+bcc structure, fracture strength and yield strength increase but elongation drastically decreases. Over 16 % of Al the alloy becomes brittle [16-17]. Precipitation hardening can be also induced by the addition of titanium [18].

In this work Classic Cantor alloy's mechanical properties were improved using low cost casting techniques and a combination of different metallurgical methodologies (heat treatment, cold working and alligation).

The alloying element use in the experimentation is tungsten (W), an element usually employed in Resistance Alloys like high quality steels (tools steels, self-hardening steels), Super Alloys (like Stellite Co-Cr) and Inconel (a nickel based alloys).

Several researchers found that this element can improve HEAs mechanical properties even if ductility reduction is observed [19-22].



EXPERIMENTAL

In this work two HEAs were investigated: a classic Cantor Alloy (CoCrFeMnNi) and a Cantor Alloy modified with the addition of W as alloying element. As raw materials, pure metals with analytic grade were used, W was added as master alloy (W85-Fe15). Raw materials were melted in a centrifugal induction furnace under argon protective atmosphere and then cast in a graphite mould in order to obtain several cylinders (diameter 12 mm, length 70 mm). The target composition for the Cantor alloy (hereinafter call Ca-Cl) is 20%_{at} for each element. The second tested alloy (hereinafter called Ca-5W) was produced employing the same quantity of materials used for the Ca-Cl alloy with a W-Fe master alloy addition (5 g). This procedure brought to a nominal composition for W of 2-3%_{at} and a little increase of the Fe concentration. The ingots were cut using a diamond blade to obtain some little samples for the microstructural analysis and the preliminary heat treatment tests and standard dog-bone samples for mechanical characterization.

In order to evaluate the effect of cold deformation on the alloys properties, some ingots were deeply cold rolled with a 50% of diameter reduction, obtaining rectangular samples. The cold rolling process was carried out only in the longitudinal direction with sample rotation in order to prevent the bending of the laminate. Each ingot composition was measured using the EDS system KEVEX-Noran System Six.

Both materials (Ca-Cl and Ca-W) were tested in the following conditions: as cast condition (Type 1), as cast + heat treatment at 1000°C for 24h (Type 2), cold-rolled (Type 3) and cold-rolled + heat treatment at 1000°C for 24h (Type 4). Comparisons and related differences were investigated and reported below.

The microstructures were characterized by optical microscope and SEM-EDS observation on sample grounded with SiC papers up to 1200 mesh, polished up to 0.3 μm alumina suspensions and electrochemical etched with oxalic acid solution at 10%, with ΔV 2.5 V, time 90 s in order to highlight microstructure characteristics.

XRD measurements were made with a Philips PW 1830 diffractometer equipped with a Philips X-PERT vertical Bragg–Brentano powder goniometer. A step–scan mode was used in the 2θ range from 30° to 100° with a step width of 0.02° and a counting time of 1.5 s per step. The employed radiation was monochromated Cu Kα.

In order to evaluate mechanical properties tensile tests were performed according to ASTM E8 standard. Proportional dog bone specimens were machined from alloy ingots. For Type 1 and Type 2 conditions tensile samples have a circular section (diameter 6 mm), for Type 3 and 4 conditions tensile tests have rectangular sections (4x6 mm). Tensile tests were carried out on an Instron 3367 dynamometer, with a load cell of 30kN, a standard electromechanical extensometer with a gauge initial length of 25 mm and a crosshead which corresponds to approximately 0.025 %/s. In addition to the tensile tests, HV₁₀ hardness measurements were used.

RESULTS AND DISCUSSION

Tab. 1 shows chemical compositions of two alloys, the reported values are the average values obtained from all the ingots. The standardized manufacturing procedure (same quantity of elements inserted in the crucible and same melting and casting time) led to ingots with almost the same compositions. EDS composition analysis has been performed on different ingot sections to evaluate the chemical homogeneity. It can be noted that the obtained chemical compositions are very close to the desired target compositions, this means that the induction melting in argon protective atmosphere didn't lead to significant material losses.

		Cr	Mn	Fe	Co	Ni	W
Ca-Cl	%at	19.81	20.93	20.03	20.35	18.88	----
	Dev.st	1.49	0.92	0.5	0.50	1.19	----
	%w	18.38	20.51	19.54	21.39	19.75	----
	Dev.st	1.40	0.88	0.58	0.52	1.24	----
Ca-W	%at	19.51	19.40	21.1	18.65	18.94	2.40
	Dev.st	0.39	0.79	0.41	1.42	0.91	0.31
	%w	17.19	18.09	20.03	18.57	18.75	7.38
	Dev.st	0.35	0.69	0.45	1.42	0.87	0.93

Table 1: Cantor Classic and Cantor alloyed with W alloys chemical compositions.

Tab. 2 shows dimensional and thermodynamic property values calculated for the two tested alloys starting from the measured chemical compositions. The main differences between the alloys are in the atomic size difference (δ) and in the

valence electron concentration (VEC). The elements selected for the Cantor classic alloys have very similar atomic dimensions (around 125 pm). Tungsten has an atomic radius much larger than the other elements (139 pm), its addition leads to a higher value of δ . Tungsten has also a higher valence electron number than the other Cantor elements. (20 vs. 6÷10) This leads to higher VEC which rises from 7.98 calculated for the Ca-Cl alloy to 8.23 for the Ca-W alloy.

	δ	ΔH_{mix} kJ/mol	T_{mix} K	ΔS_{mix} J/mol K	Ω	e/a	VEC
Ca-Cl	0.80	-3.74802	1798.562	13.38	6.42	2.20	7.98
Ca-W	1.81	-3.68568	1847.82	13.99	7.02	2.19	8.23

Table 2: Dimensional, thermodynamic and electronic parameters.

HEAs theoretical rules [23] state that for a solid solution realization the mixing entropy ($T\Delta S_{mix}$) should be greater than the mixing enthalpy (ΔH_{mix}); this condition is obtained when their ratio ($\Omega = T_{mix}\Delta S_{mix} / \Delta H_{mix}$) is greater than 1. Also δ is important in order to define HEAs phase stability. Low δ values (similar atomic radii of the alloys elements) promote the formation of a solid solution. Usually HEAs, characterized by a solid solution microstructure, have ΔS_{mix} in the range 12÷17.5 J/mol K, δ lower than 6.6 and ΔH_{mix} higher than -15kJ/mol ($\Omega \geq 1.1$). The calculated values of these thermodynamic and dimensional parameters for both Ca-Cl and Ca-W alloys predict the formation of a solid solution. VEC and e/a are parameters usually employed to predict the kind of crystalline structure. The recent research seems to state that VEC is the more straightforward parameter to be used for the HEAs alloys containing mainly transition elements [23]. Up to now accepted relationship between VEC and crystallographic parameters establishes that the solid solution is characterized by body centred cubic lattice (bcc) up a VEC value of 6.7, over 8 VEC structure is characterized by a face centred cubic lattice (fcc), between these value range a mixture of bcc and fcc can be detected. Both the manufactured alloys should be characterized by a fcc lattice. Summing up, from the calculated parameters it can be asserted that both Ca-Cl and Ca-W manufactured alloys should be characterized by a monophasic fcc solid solution.

Microstructural analyses were carried out on several specimens for both compositions, analyzing from Type 1 up to Type 4. Figures show the microstructure of Ca-Cl Cantor Classic (Fig. 1a) and Cantor Ca-W (Fig. 1b) casted alloys (Type 1), where grain structures are similar, in Cantor Ca-W tungsten areas can be observed.

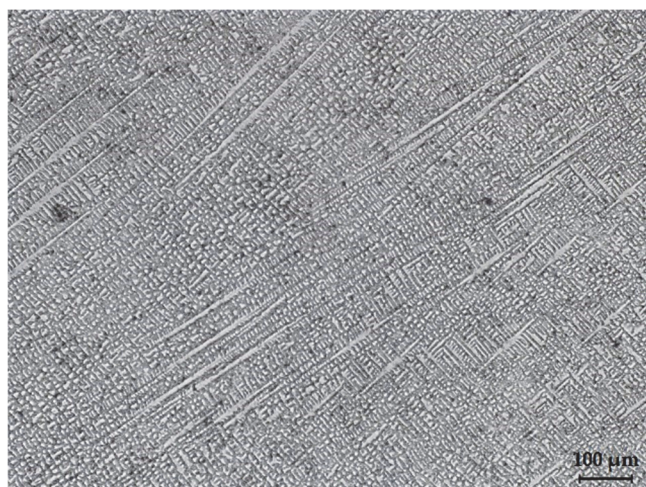


Figure 1a: Dendritic structure of As Cast (Type 1 condition) Ca-Cl alloys

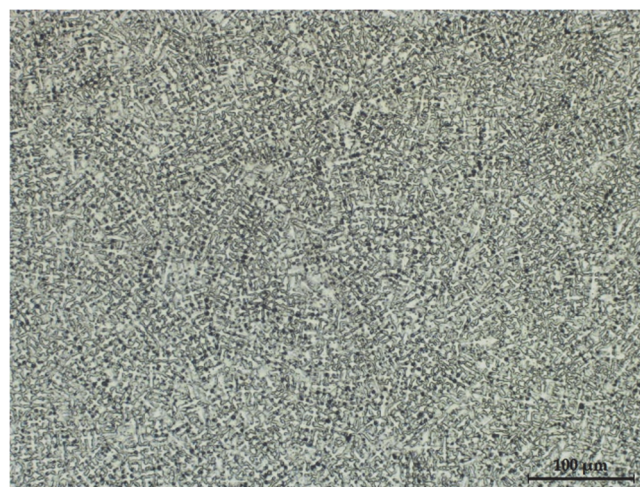


Figure 1b: Dendritic structure of As Cast (Type 1 condition) Ca-W alloys

The analysis highlights that Ca-Cl and Ca-W samples show similar morphological aspects. The microstructures characteristics change with manufacturing processes.

Type 1 samples show a typical dendritic microstructure of as cast alloy (Fig. 1a and 1b respectively). The dendritic structure is finer in the Ca-W sample then in the Ca-Cl one. In the Ca-W alloy sporadic W inclusions were observed (Figg. 2a and 2b). This suggests using a longer melting time to complete the melting process of tungsten which has the higher melting point.

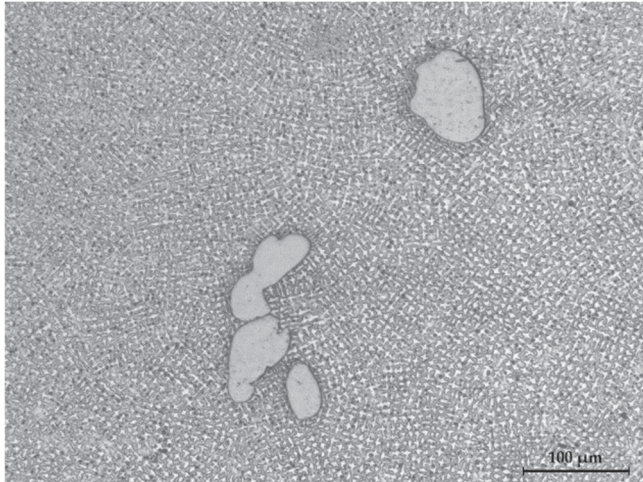


Figure 2a: W inclusion in 5 Type 1 Ca-W samples (optical micrograph).

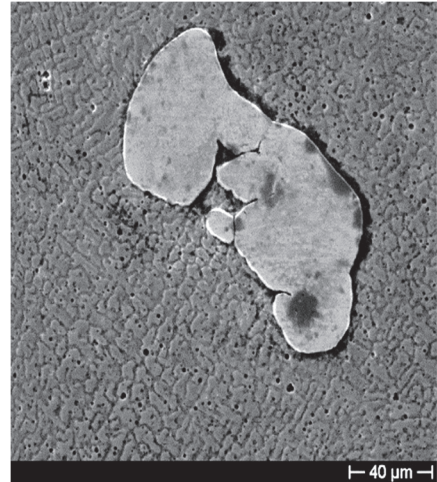


Figure 2b: W inclusion in 5 Type 1 Ca-W samples (SEM micrograph).

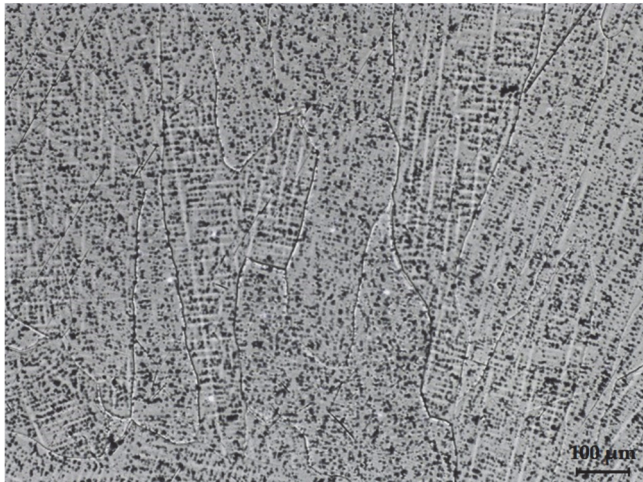


Figure 3a: Grain structure of Type 2 Ca-Cl sample.

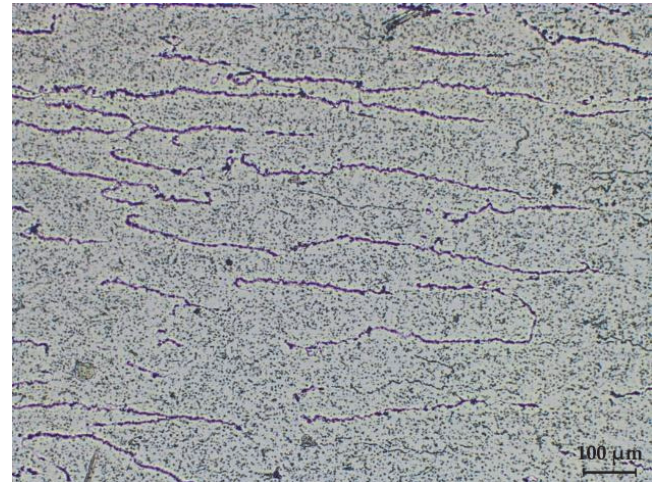


Figure 3b: Grain structure of Type 2 Ca-W sample.

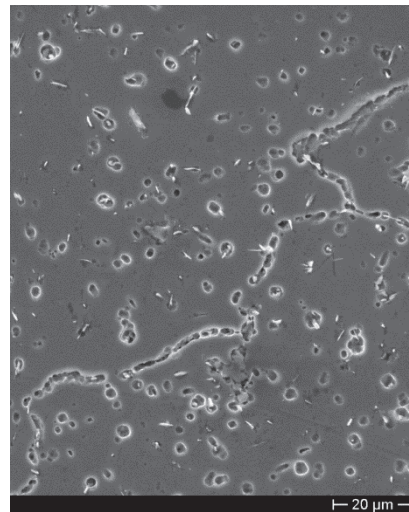


Figure 3c: SEM micrograph of Type 2 Ca-W sample.

After heat treatment at 1000°C for 24 hours, the dendritic structure observed in Type 1 (as cast condition) tends to disappear in Type 2 (as cast + heat treatment at 1000°C for 24h) where coarse grains were observed (Fig. 3a), with a columnar structure near the edge of the ingots, equiaxed in sample central part. In Ca-Cl Type 2 sample, after the metallographic etch, the grain boundary appears as fine dark point lines. Inside the grain are still visible the dendritic structures of the as cast condition. After the metallographic etch in Ca-W samples the grain boundary is more evident than those of Ca-Cl type 2 samples. Grain Boundary appears as a series of coarse black dots, no dendrites were observed inside the grains (Fig. 3b). Fig. 3c shows a SEM micrograph of the grain boundary of Ca-W Type 2 etched sample. The grain boundary appears as a line of small holes, a white bright phase appears and the EDS analysis reveals that it is rich in W (probably the intermetallic phase Fe_7W_6).

Laminated materials (Type 3 condition) show similar structures (Fig. 4a and b). After metallographic etch no dendrites were observed. Fine grain boundaries were detected (Fig. 4a) similar to those of Ca-Cl Type 2 alloys (Fig. 3a). Inside grains the metallurgical etch highlights the flow lines developed during the cold working process, they appear as parallel waves perpendicular to the lamination direction (Fig. 4b).

Laminated and heat-treated material microstructure (Type 4) is completely different (Fig. 5a and b). Austenitic grain geminated structures are also observed. In the Type 4 Ca-W alloy, a fine dispersion of white bright intermetallic particles (fig 5c) is present. EDS analysis highlights the particles could be the intermetallic Phase Fe_7W_6 .

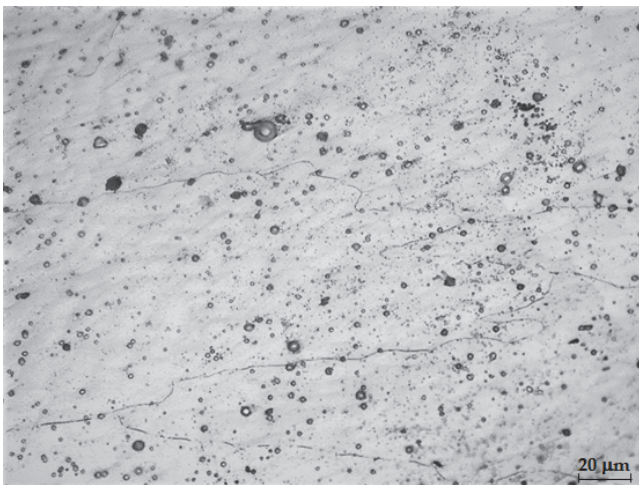


Figure 4a: Grain structure of Type 3 Ca-Cl sample.

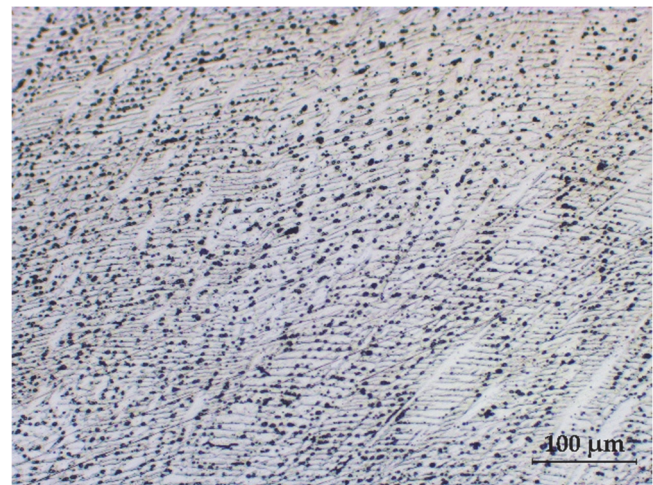


Figure 4b: Grain structure of Type 3 Ca-W sample.

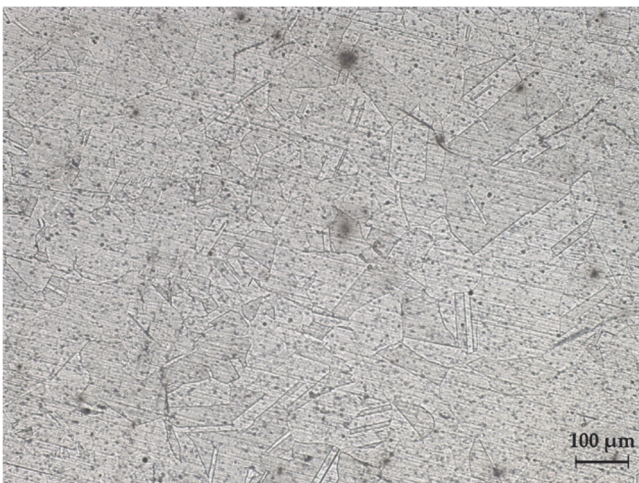


Figure 5a: Grain structure of Type 4 Ca-Cl sample.

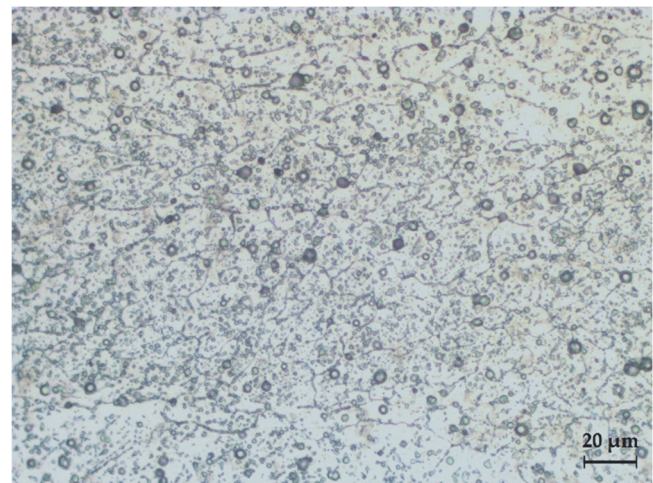


Figure 5b: Grain structure of Type 4 Ca-W sample.

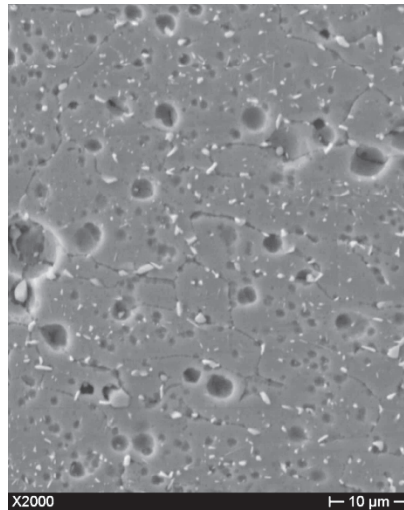


Figure 5c: SEM micrograph of Type 4 Ca-W sample,

The comparison between Type 1 Ca-Cl (in blue) and a Type 1 Ca-W (in red) XRD diffractograms are reported in Fig 6 , where a single-phase signal of the fcc structure of the two alloys is detected. A light shift of the Ca-W diffractogram is observed, due to Tungsten addition that acts a small variation of cell parameters according to Vegard's law [24]. The observation of the diffractograms of the Ca-W Type 2 and the Type 4 (Fig 7), both heat treated, show some small intensity peaks located at the left part of the diffractograms that can be associated with the presence of intermetallics formed during the heat treatment, as seen in the SEM observation. The study of these peaks can be likely attributed to Fe7W6 (ICDD PDF #42-1209).

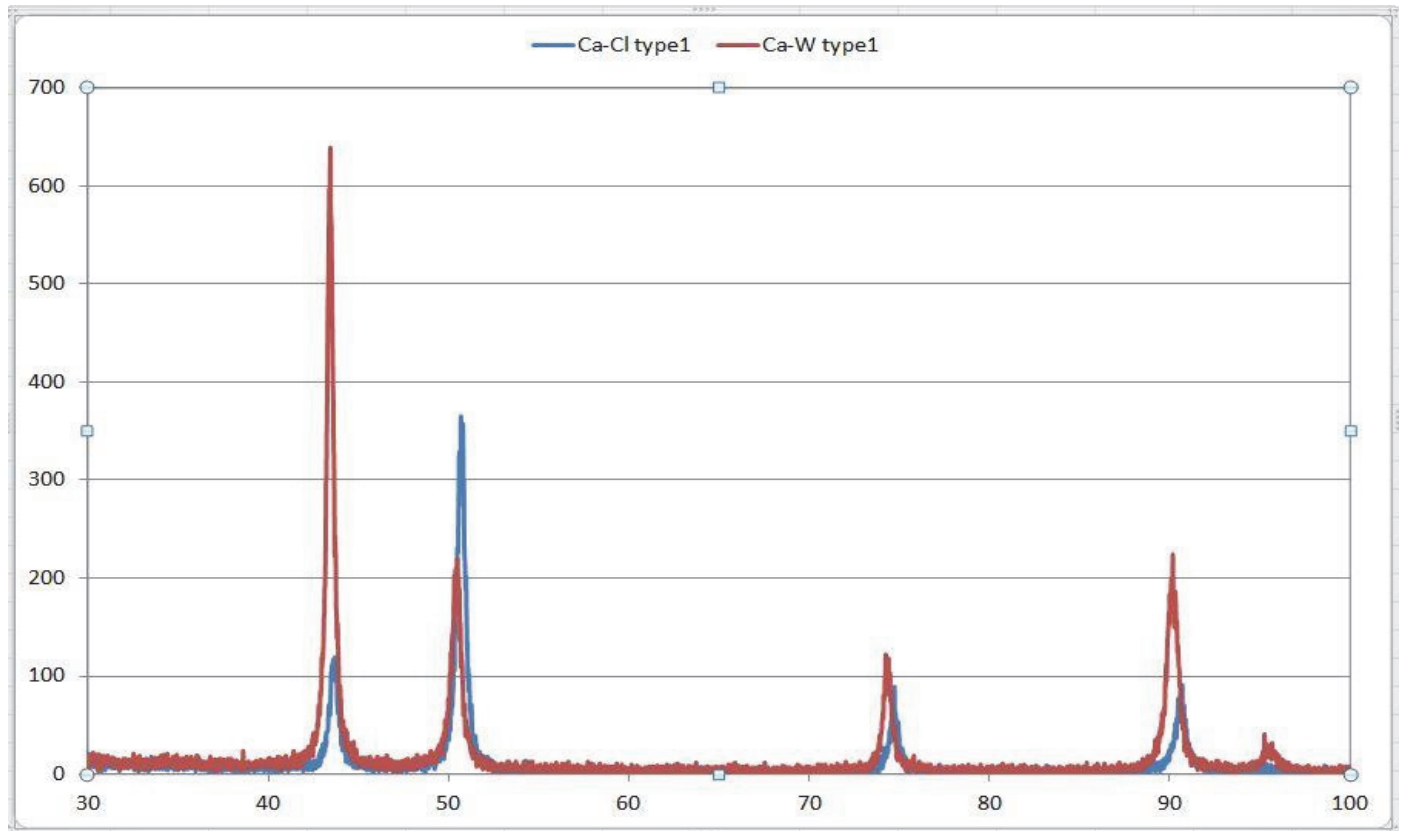


Figure 6: XRD spectra confrontation: Ca-Cl type 1 (in blue) and Ca-W type 1 (in red).

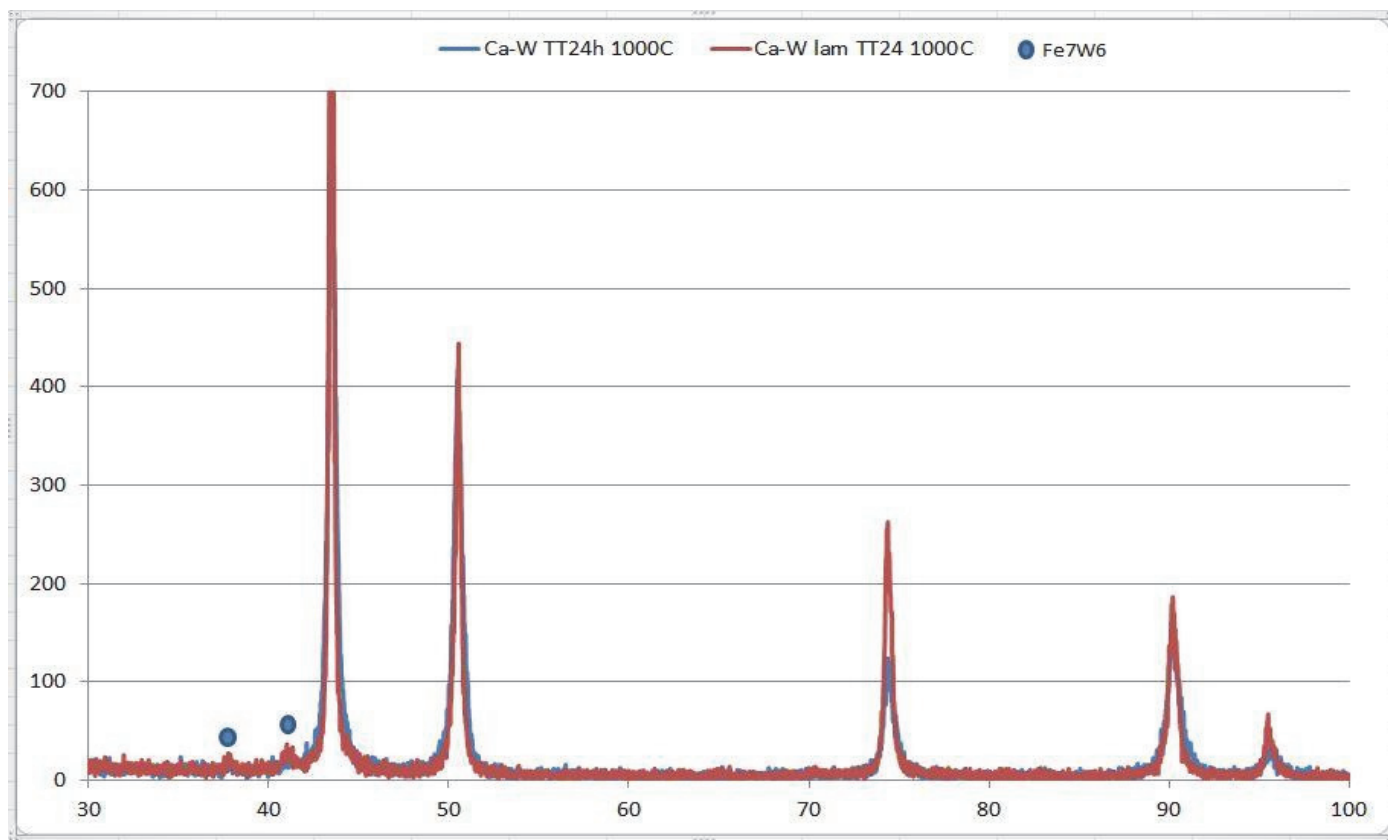
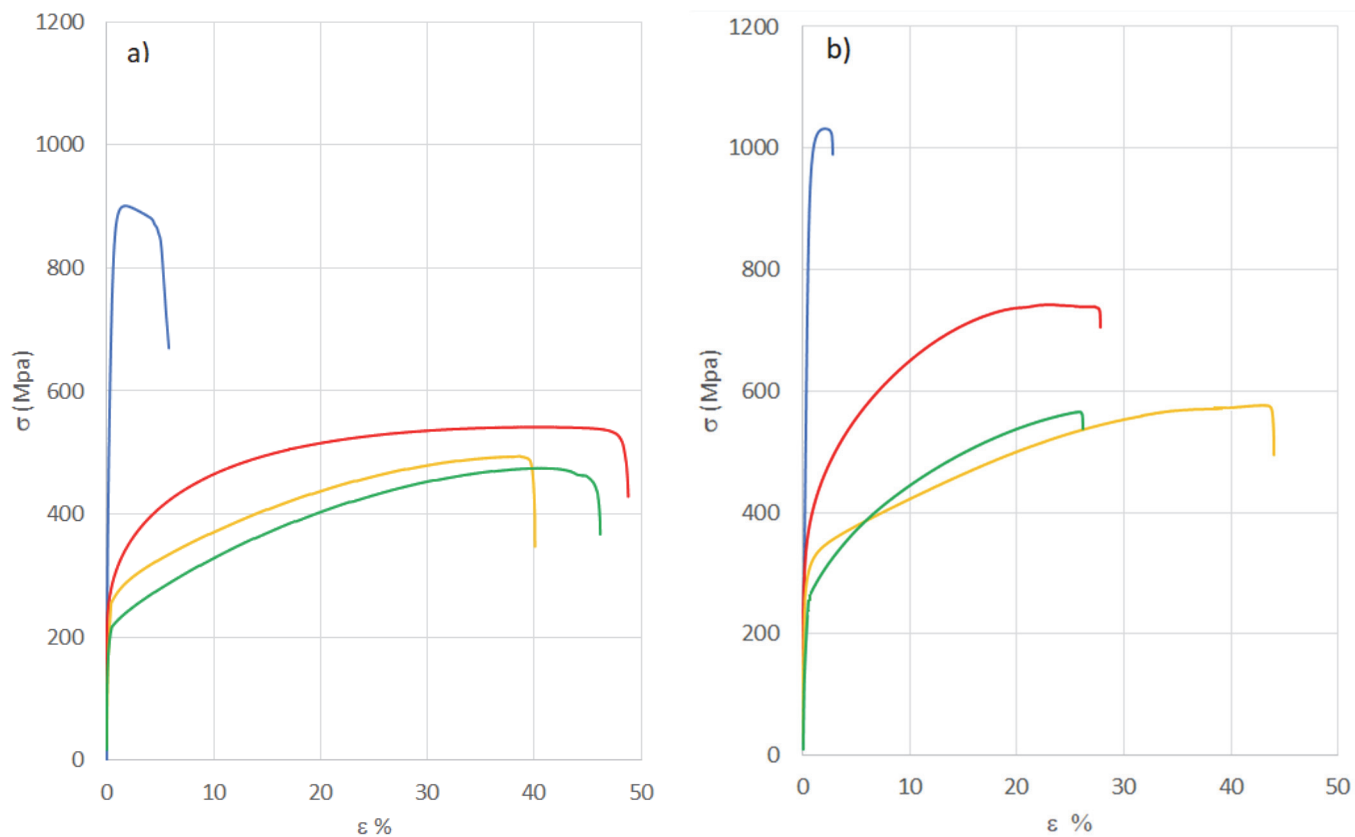


Figure 7: XRD spectra confrontation: Ca-W TT 24h 1000°C (in blue) and Ca-W Lam TT 24h 1000°C (in red).



Figures 8: Tensile test curves of Ca-Cl (a) and Ca-W (b): yellow as cast (Type 1); green as cast+ heat treatment at 1000°C for 24 hours (Type 2); blue laminated (Type 3); red laminated + heat treatment at 1000°C for 24 hours.



Figs. 8 a and b show the tensile test curves of the tested materials. Mechanical properties are reported in Tab. 3. Both Ca-Cl and Ca-W show a similar trend in function of the manufacturing conditions with little difference between them. The following consideration can be done.

Alloying with tungsten leads to an increase of HV, Ultimate tensile Strength (U.T.S.) and Yield Stress (Y.S) and in a reduction of the breaking elongation (A%) after heat treatment.

Alloy	Condition	HV10-15	U.T.S.	Yield	Elongation
			MPa	MPa	A%
Ca-Cl	Type 1	154	495	255	40
	Type 2	149	474	215	46.2
	Type 3	354	901	869	5.8
	Type 4	185	541	205	48.8
Ca-W	Type 1	155	573	288	41.2
	Type 2	182	564	277	33
	Type 3	367	1031	931	2.6
	Type 4	230	739	350	27.8

Table 3: Cantor Classic and Cantor Ca-W alloys mechanical properties.

Heat treatment of the as cast alloys (Type 2) produces in both cases a little reduction of strength and yield. For the Ca-Cl also HV decreases, while A% slightly increases. This indicates that there is a general softening of the material probably due reduction of internal tensions and an initial homogenization process. These results are compliant with the microstructure analysis which highlight only minor modification of the dendritic structure which characterises the as cast materials. On the contrary the heat treatment of the as cast Ca-W alloy results in a sensible reduction of the A% and in a strong increase of HV. In effect the microstructure of as cast Ca-W is deeply modified by the heat treatment. The dendritic structure disappears and the grain boundary is characterized by precipitation of an intermetallic second phase. This precipitation could bring to the observed reduction of the A%.

Deep cold lamination process (Type 3) brings to a work hardened microstructure with mechanical properties strongly increased. Obviously, the elongation is almost zeroed.

The combination of deep cold working and heat treatment (Type 4) brings a better combination of resistance and plasticity for both the alloys. Strength (HV and U.T.S.) and plasticity (higher elongation and lower yield stress) of the Ca-Cl Type 4 alloy increase respect to the as cast properties. The manufacturing procedure completely modifies the microstructure which is completely recrystallized. The internal shrinkage defects observed in the as cast specimens (also in the heat treated as cast samples) are significantly reduced.

The Ca-W alloy shows a different behavior. The strength properties increase is much higher than those measured for the Ca-Cl alloys. HV and U.T.S are more than 45%, higher respect to the value obtained in the Type 1 Ca-W alloy. Instead, the plasticity is reduced. Yield stress increases (40%) and elongation is reduced (-30%). This behavior, different from those observed for Ca-Cl material, is probably due to a not complete recrystallization process and to the precipitation of the intermetallic tungsten phase. The fully recrystallized microstructure which characterizes Type 4 Ca-Cl materials (regular f.c.c. grain with geminates inside) is not observed in Ca-W Type 4 samples.

For them, grains are finer than those observed in as cast sample, but their shape is not regular, and the grain boundary seems more similar to those observed in as cast and heat treated as cast sample (dotted line). No geminates were observed. There is also a remarkable intermetallic precipitation.

The fractographic analysis of both Ca-Cl and Ca-W samples in all the tested conditions show the same results. The morphology of the fracture surfaces is independent from the W allegation or the thermo/mechanical treatment. It is characterized by a fine dimple network (Figs. 9 a-d).

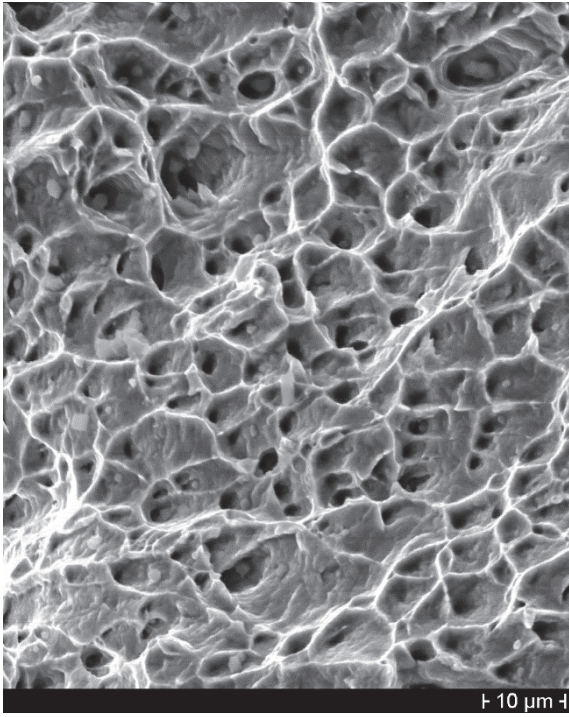


Figure 9a: SEM micrograph of the fracture surface of Ca-Cl type 2 tensile test sample.

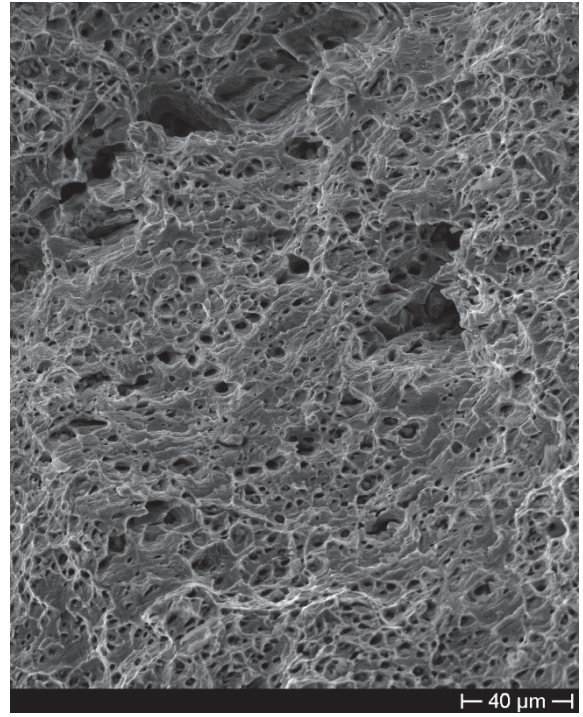


Figure 9b: SEM micrograph of the fracture surface of Ca-Cl type 2 tensile test sample.

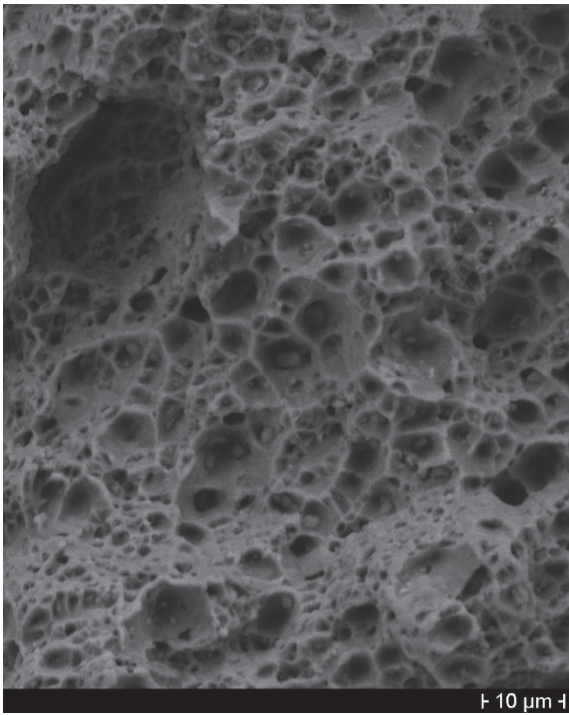


Figure 9c: SEM micrograph of the fracture surface of Ca-W type 4 tensile test sample

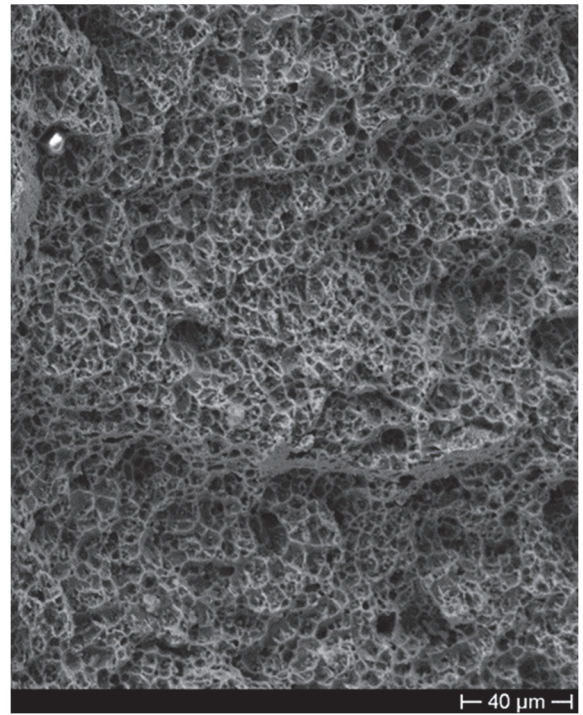


Figure 9d: SEM micrograph of the fracture surface of Ca-W1 type 2 tensile test sample



CONCLUSIONS

The present work addressed the following results:

- The possibility to realize Cantor alloys with low-cost production techniques, able to use this material in different engineering fields.
- The Tungsten alligation improves mechanical characteristics in all 4-Type tested Cantor alloys. This element is usable, as well known in steel production, also in HEAs manufacturing.
- Heat treatments improve ultimate tensile stress as well as enervation properties only after deep lamination procedures. This lamination produces a material deep hardening and a general reduction of internal defects which arise from cast procedures. Subsequent heat treatments generate grain refinement in the alloys.
- In Cantor alloys with tungsten heat treatments produce intermetallic precipitations (Fe_6W_7) in grain boundaries.
- The deep lamination process (Type 3 condition) leads to the highest values of U.T.S. and Yield Strength, while it reduces drastically the elongation (A%)
- W alligation reduces the elongation (A%)
- The properties of Cantor type HEAs can be easily modified through alligation and/or thermo-mechanical treatments in order to maximize the strength characteristic or the plastic behavior (ductility).

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