Al0.5CrCoFeNi high entropy alloy for Geothermal Environment

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Abstract. Al0.5CoCrFeNi high entropy alloy was processed by mechanical alloying and investigated in term of powders characteristics and microstructures. The obtained power was pressed and sintered resulting in a bulk material that will be further processed to obtain electrodes that will be deposited on the substrate by electro spark deposition process, in an attempt to obtain a corrosion resisting coating. High Entropy Alloys are known due to their corrosion and wear resistant properties, which makes them the perfect candidates in numerous domains as marine, geothermal, oil and gas industries, where the aggressive environment tends to corrode the in work components of the equipment. The cocktail effect is characteristic to the high entropy alloys, where every component concurs in an alloy with predetermined properties.

1. Introduction
Energy production from geothermal resources represents a challenge due to the geothermal steam chemistry, which mainly consists of oxygen ( minimal due to reducing environment), hydrogen sulphide (H2S), carbon dioxide (CO2) and ammonia (NH3), this negatively influence the performance and durability if the in work components.

Geothermal steam is transported to the geothermal power plant, to run the turbines in order to obtain electrical power. Stainless steel is normally used in the manufacture of the turbine, due to the good corrosion resistance. However overtime, the effect of steam on the turbine blades (Figure 1) ease the degradation, this leading to the requirement of advanced materials, with superior corrosion-erosion resistance, to counter the aggressive environment [1].

High entropy alloys are multi-element alloys, equiatomic or near equiatomic, with a structure consisting in solid solutions with BCC or/and FCC phases. HEAs are known for high hardness, strength, good wear resistance, corrosion and oxidation resistance [2-4, 18].

Figure 1. Corrosive effect on the current turbine blades used in the geothermal power plant.
According to literature [5-11], the cocktail effect, severe lattice distortion and sluggish diffusion, which are characteristic effects of the high entropy alloys, result in wear, oxidation and high corrosion resistance and excellent mechanical properties at high temperatures.

Al_{0.5}CoCrFeNi high entropy alloy was obtained by mechanical alloying and further pressed, sintered and mechanical machined into electrodes, in order to be deposited on the substrate by electro spark deposition process.

2. Experimental procedure

Al_{x}CoCrFeNi high entropy alloy is one of the most widely researched alloy systems [13-16]. According to Wang et al. the Al concentration results in hardness increase of the alloy.

For this paper, Al_{0.5}CoCrFeNi was selected due to its known corrosive and wear resistance properties. The material benefits from the cocktail effect and for our experiments we use high purity raw materials of Al, Co, Cr, Fe and Ni which were placed in the planetary mono-mill (Figure 2). For the milling process we used with stainless steel vials and balls, ball to powder ratio of 10:1 and N-Heptane as a process control agent with a milling time of 275 min. Wet milling with n heptane was preferred due to the good results obtained in previous experiments [17]. Wet milling prevents welding with the vial walls and helps the powder particles to weld and be crushed again repetitively to ensure a homogeneous mechanical alloying process. The rotational speed used for the mechanical alloying process was 350 rpm.

Mechanical is an more economical process compared to the other processes that might be used in order to obtain this alloy, a completely solid state processing technique, with vast potential where the mechanically alloyed powders produce multiple metastable phases. This alloy is suitable for processing in solid state due to the component powders stability. The vacuum arc remelting processing could be more difficult due to the low melting point of aluminum powder [4, 12].

![Figure 2. Fritch planteray mono mill used for the experiments](image)

![Figure 3. Substrate:a) before coating; b) after coating.](image)
After the mechanical alloying, the material was pressed and sintered in order to obtain a bulk material that will be further processed in order to obtain electrodes. The powder was pressed using a uniaxial press with 15tf and the sintering was realized in argon atmosphere, at 800°C for 1h. The heating rate was 10°C/min and the sample was cooled in the furnace after the sintering process.

The obtained electrodes were used to coat the substrate by electro spark deposition process, with a miniature applicator. The coating was obtained by depositing multiple layers on the substrate surface (Figure 3).

3. Results and discussion
The microstructure obtained for the initial powders used for solid state processing of Al0.5CrCoFeNi are presented in Figure 4. The EDS analyses results confirmed the composition of each powder.
Figure 4. Microstructure analyses and EDS analyses result for the component powder of solid state processed high entropy alloy.

In Figure 4 we can observe that Al powder is homogeneous but the powder particles have different shapes from spherical to cuboidal. For Co, Cr, Fe the particles have cuboidal shape and Ni has a spherical shape. The EDS confirmed the composition for each powder analyzed. The powder dimensions varied between 45 µm (Fe, Co) to 63 µm (Al, Cr, Ni).

The powders were homogenized for 30 minutes in the planetary ball mill and a sample was taken and denoted HEA_0 as a reference before milling. The sample was collected before adding heptane in the mixture. After 275 min milling a sample was collected as well and denoted with HEA_A.

The microstructures of the samples collected before and after milling are presented in Figure 5. The EDS analyses results confirmed the composition of the high entropy alloy processed in solid state.

In Figure 5 all the powder particles from the Al_{0.5}CrCoFeNi alloy could be identified by its specific shape. Al particles could be observed, similar with Figure 4 Al, Ni particles could be easily identified being the spherical one. After 275 milling the powders particles have polygonal shape and uniform color suggesting that alloying process was produced. The characteristics for HEA_A powder obtained after mechanical alloying were determine to characterize the high entropy alloy processed in solid state.

The value of the free flow density was 2.403 g/cm³ and the tap density experimentally determined using the hall flowmeter was 3.378 g/cm³. The packing density representing the ration between free flow density and tap density is 71% which is a good value for a powder. The packing density indicates the ability of the powder to be further process by pressing and sintering and a good value should be comprise between 65 and 75%.

Using a Carney funnel the flow rate was determined to be 2.87 g/s and the tap angle was also determined. The value calculated for the tap angle was 20.16 degree. A good flowing of the powder is found to be at angles below 35 degree [12]. The value obtained for Al_{0.5}CrCoFeNi is good for the
flowing rate indicating that the powder could also be used for coatings using different procedures as high velocity oxygen fuels spraying.

![Microstructure and EDS analyses results for HEA_0 (a, b) and HEA_A(c, d).](image)

The XRD diffraction pattern is presented in Figure 6. The XRD pattern reveals the disappearing of the single phase’s peaks in the HEA_A pattern and broadening of the peaks indicating that the alloying process produced. The calculated valence electron concentration value was 7.725 and the value was determined using the formula (1).

\[
VEC = \sum_{i=1}^{n} c_i VEC_i
\]  

Where VEC\(_i\) is the valence electron concentration of each component and \(c_i\) is the concentration of each component of the Al\(_{0.5}\)CrFeNiMn high entropy alloy [19]. According to Guo et all [19] if the VEC value is comprised between 6.8 and 8 the high entropy alloy obtained will contain a mixture of phases. In our chase the dominant phase is FCC with some amount of BCC phase present in the structure.

We further process the Al\(_{0.5}\)CrCoFeNi high entropy alloy using uniaxial pressing and sintering in argon atmosphere. The microstructure of the sample after pressing and sintering is shown in Figure 7. The EDS analyses reveal the fact that no oxygen contaminated the samples. The powders were handled in the glove box in argon atmosphere and the sintering was also produced in argon atmosphere.
Figure 6. XRD pattern for the homogenized sample (HEA_0) and alloyed sample (HEA_A).

Figure 7. The microstructure of the Al_{0.5}CrCoFeNi high entropy alloy produced in solid state and EDS analyses results.

The microstructure of the consolidated powder reveals a homogeneous structure with two phases present and some compound segregating at the grain boundaries. The structure obtained allowed us to cut the sample in a cylinder shape to produce the electrode for electro-spark deposition process.
4. Conclusions
A high entropy alloy with the composition Al_{0.5}CrCoFeNi was produced by mechanical alloying, pressing and sintering to produce an electrode for electro–spark deposition process.

The powder obtained was characterized in terms of packing density, tap angle and flow rate. The values obtained for Al_{0.5}CrCoFeNi high entropy alloy are encouraging for further processing this alloy. The flowing rate had a good value, tap angle were 20.16 degree indicating also a good flowing rate. The packing density was determined to be 71%. The calculated valence electron concentration was 7.725 indicating a mixture between FCC and BCC phases, confirmed by the XRD pattern on the mechanically alloyed sample. The pressing and sintering process resulted in a good, compact sample used for this alloy was 800°C.

The samples were also investigated from microstructural point of view underling the phases changing and the alloying process for Al_{0.5}CrCoFeNi high entropy alloy. Our future goal is to produce a coating using the obtained electrode and to expose the coated sample in geothermal steam to investigate the Al_{0.5}CrCoFeNi behavior in aggressive environments.

5. References
[1] Nogara J and Zarrouk S J 2018 Renewable and Sustainable Energy Reviews 82 1333–46
[2] Chen W, Fu Z, Fang S, Xiao H and Zhu D 2013 Materials and Design 51 854–860
[3] Ji W, Wang W, Wang H, Zhang J, Wang Y, Zhang F and Fu Z 2015 Intermetallics 56 24-27
[4] Matara M A, Csaki I, Popescu G, Popescu C A, Soare V, Soare A and Mitrica D 2015 U.P.B. Sci. Bull., Series B 77 351-358
[5] Tsai M H and Yeh J W 2014 Mater. Res. Lett. 2 107–123
[6] Wu J M, Lin S J, Yeh J W, Chen S K, Huang Y S and Chen H C 2006 Wear 261 513–519
[7] Lee C, Chang C, Chen Y, Yeh J and Shih H 2008 Corros. Sci. 50 2053–60
[8] Chuang M H, Tsai M H, Wang W R, Lin S J and Yeh J W 2011 Acta Mater. 59 6308–17
[9] Zhao J H, Ji X L, Shan Y P, Fu Y and Yao Z 2016 Mater. Sci. Technol. 1–5
[10] Lee C, Chen Y, Hsu C, Yeh J and Shih H 2008 Thin Solid Films 517 1301–05
[11] Naira R B, Aroraa H S, Mukherjeeb S, Singhc S, Singhc H and Grewala H S 2018 Ultrasonics-Sonochemistry 41 252–260
[12] Suryanarayana C 2001 Mechanical alloying and milling 46 1-184
[13] Ellis P 1985 Companion study guide to short course on geothermal corrosion and mitigation in low temperature geothermal heating systems (Austin, Texas: Radian Corporation)
[14] Matsuo K 1973 Drilling for geothermal steam and hot water Geothermal energy: review of research and development, HCH Armstead, editor, UNESCO. ISBN 92-3-101063-8
[15] MR0175 NACEI 2009Petroleum and natural gas industries-Materials for use in H2Scontainingenvironments in oil and gas production Part 1
[16] Finger J and Blankenship D 2010Handbook of best practices for geothermal drilling (Albuquerque: Sandia National Laboratories) 1344
[17] Csaki I, Stefanious M, Geanta V, Voiculescu I, Sohaciuc M G, Soare A, Popescu G and Serghiuta S 2018 REV.Chim. (Bucharest) 67(7) 1373 - 1377
[18] Fan Q C, Li B S and Zhang Y 2014 Journal of Alloys and Compounds 614 203–210
[19] Guo S, Ng C, Lu J and Liu CT 2011 J. Appl. Phys. 109 1–6

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