Comparative microstructural and corrosion development of VCrNiCoFeCu equiatomic multicomponent alloy produced by induction melting and spark plasma sintering

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Abstract. The present study focuses on the corrosion behavior of a single-phase FCC high entropy alloy (VCrNiCoFeCu) casted by two different methods: induction melting and spark plasma sintering. The corrosion resistance has been evaluated using immersion tests in 3.5% NaCl solution, the potentiodynamic polarization measurements and the results are compared how is dependent the corrosion rate as a function of the production methods. Our results show that induction melted sample is stable in salty environment. On the other hand, based on the changes of polarization curves, there must be an evolution of oxide films on the SPSed sample until reaching the stable oxide layer.

1. Introduction
Traditional concept of alloy systems has been based on utilizing one or two elements as the principal components, and sometimes, minor quantities of other elements are used to enhance the properties, such as steels, NiAl intermetallics and bulk metallic glasses (BMG) [1]. The main reason is that traditional metallurgical knowledge suggests that complex phases or intermetallics will be easily formed in alloy systems with multiple principal components, and thus lead to poor mechanical properties [2].
In the last decade, the so called High-Entropy Alloys (HEAs) became popular materials because of their unique properties, as high strength and ductility simultaneously [1–3], thermal stability [4–6] and excellent corrosion resistant properties [7–9].
The name comes from the fact that high mixing entropy $\Delta S_{\text{mix}}$ can dominate the term of Gibbs relation: $\Delta G_{\text{mix}} = \Delta H_{\text{mix}} - T \Delta S_{\text{mix}}$. High entropy comes from the high number of elements in the alloy, since based on the definition as an alloy HEA system is composed of five or more kinds of principal elements in an equimolar or near equimolar ratio, with a small difference in atomic radii (<15%) and concentration of each element is varying from 5 to 35 at%. By this way the significance of the enthalpy of mixing ($\Delta H_{\text{mix}}$) is oppressed and the solid solution phase is favoured over the intermetallic phases. This explanation and the name HEA came from Yeh and co-workers from year 2004 [10,11]. With proper composition designing, the HEA exhibits high hardness, excellent ductility as well as promising resistances to wear, oxidation and corrosion [5].
In this paper, we investigate VCrNiCoFeCu high-entropy alloy prepared by induction melting and spark plasma sintering methods. We conducted this comparative analysis for the two methods because the induction melting is not the best for industrial manufacturing due to the diseconomy and limitations in shape and size of final products. By contrast, mechanical alloying (MA) is a more convenient way, which has been widely used for the synthesis of nanocrystalline materials and widens the application scope of HEAs [6,7]. In addition, combined with the novel Spark Plasma Sintering (SPS) technique, bulk metallic glasses and high-entropy alloy can be easily obtained from the as-milled powders [8,9].

2. Experimental procedures

Metal powders of V, Cr, Ni, Co, Fe, Cu with purities of higher than 99.5 wt% and particle size ≤45 µm were used as initial materials. The elemental powders were mixed in equiatomic composition and milled in planetary ball miller (Fritsch pulverisette-4) for 20 h at 400 rpm in an argon atmosphere.

The obtained powder mixtures were sintered under vacuum using an SPS system (FCT System HPD 25). The sintering temperature was measured (0.05K precisely) and controlled by a thermocouple inserted into the graphite die wall at a distance of about 2 mm from the sintered sample. A uniaxial pressuring method was conducted using top and bottom graphite punches. The loading pressure was 90 MPa. A heating rate of 100 K/min was applied from room temperature to 480 °C before slowing down to 20 K/min from 480 °C to 500 °C to avoid temperature overshoot. The sintering temperature ranged from 500 to 550 °C. The holding time at the sintering temperature was in the range 20–30 min. Then the sample was removed from the heated region and a natural cooling was applied so that after about 30 min the specimen was at room temperature. The densified samples had a cylindrical shape, with a diameter of about 10 mm and a thickness of about 4 mm. All characterizations have been realized on these cylinders.

In the case of induction melting, lumps of high purity (99.99%) elements were melted under protecting atmosphere of argon to prepare the VCrNiCoFeCu equi-molar composition alloy.

The Scanning Electron Microscopy (SEM) was taken on FEI Quanta 3D FEG and Zeiss JSM microscopes equipped with Energy Dispersive Spectroscopy (EDS) and also Electron Back Scattered Diffraction (EBSD) instruments of EDAX.

The microstructure was investigated by electron backscatter diffraction (EBSD) using an FEI Quanta 3D scanning electron microscope (SEM). Before the EBSD investigation the surface was mechanically polished with 400, 600, 800, 1200, 2400 grit SiC abrasive. Finally, the surface was polished by 1 µm diamond paste.

The chemical composition was examined by energy-dispersive X-ray spectroscopy (EDS) in SEM.

The structure of the alloy was identified by X-ray diffraction with Copper Kα (wavelength, λ=0.15418 nm) radiation in 0–20 mode scanning from 20° to 80° at a scanning rate of 0.5°/min. For identification of the consistent phases, the PDF database was used. The average lattice parameter was determined by extrapolating the lattice parameters obtained from the different reflections to the diffraction angle of 2Θ= 180° using the Nelson–Riley method [12].

The corrosion resistances of the alloys were evaluated by polarization corrosion method. Potentiostatic polarization curves were measured with 10mV/min scan rate in 3.5% sodium chloride solution (NaCl) at 25 °C in three-electrode electrochemical cell using a 20x5 mm polycrystalline Pt wire working electrode and an Hg/HgCl₂/KCl reference electrode. The Tafel curve measurements were carried out using Zahner potentiostat. Electrochemical characteristic parameters, such as electrochemical corrosion potential (Ecorr), corrosion current density (jcorr), can be obtained by evaluating polarization curves.

3. Results and discussion

3.1. Theory analysis and discussion

In this paper the enthalpy of mixing, atomic-size difference and the parameter Ω for the multi-component VCrNiCoFeCu alloy were calculated using the following equations [13-14]:
\[ \Delta H_{\text{mix}} = \sum_{i=1, j=1}^{n} \Omega_{ij} c_i c_j \]  
(1)

\[ \Delta S_{\text{mix}} = -R \sum_{i=1}^{n} c_i \ln c_i \]  
(2)

where \( \Omega_{ij} = 4\Delta H_{\text{mix}}^{\text{AB}} \) is the regular melt-interaction parameter between \( i \)th and \( j \)th elements, \( c_i \) and \( c_j \) are the \( i-j \) atom concentrations, and \( \Delta H_{\text{mix}}^{\text{AB}} \) is the mixing enthalpy of binary liquid alloys (the value can be obtained in [10-13]).

\[
\text{Delta}(\delta) = \sqrt{\sum_{i=1}^{n} c_i (1 - r_i / \bar{r})^2}
\]  
(3)

where \( n \) is the number of the components in the alloy system, \( c_i \) is the atomic percentage of the \( i \)th component, \( \bar{r} = \sum_{i=1}^{n} c_i r_i \) is the average atomic radius, and \( r_i \) is the atomic radius which could be obtained from [14-15].

The parameter \( \Omega \) is defined to predict the solid-solution formation for various multi-component alloys as:

\[ \Omega = \frac{T_m \Delta S_{\text{mix}}}{|\Delta H_{\text{mix}}|} \]  
(4)

The melting temperature of \( n \)-elements alloy, \( T_m \), is calculated using the rule of mixtures:

\[ T_m = \sum_{i=1}^{n} c_i T_{m,i} \]  
(5)

Here, \( (T_{m,i}) \) is the melting point of the \( i \)th component of alloy. As analyzed above, the value of \( \Omega \) is positive, and \( \Omega = 1 \) should be proposed as a critical value to form a solid solution. If \( \Omega > 1 \), the contribution of \( T \Delta S_{\text{mix}} \) will exceed that of \( \Delta H_{\text{mix}} \) for a solid-solution formation. If \( \Omega \leq 1 \), \( \Delta H_{\text{mix}} \) is the dominant part in the equation, and formation of intermetallic compounds are expected [11]. In the case of VCrNiCoFeCu alloy this value is \( \Omega = 15.3 \). Considering the small atomic size differences and that the value of \( \Omega \) is larger than 1 indicates that the strain energy caused by lattice distortion is lower in VCrNiCoFeCu alloy and the entropy effect of \( \Delta S_{\text{mix}} \) is large enough to exceed the \( \Delta H_{\text{mix}} \). Thus, the component atoms can randomly distribute in the alloy and a simple solid solution is stable [15].

**Table 1.** Calculated thermodynamic parameters of the VCrNiCoFeCu High Entropy Alloy.

| Thermodynamic parameters | VCrNiCoFeCu |
|--------------------------|-------------|
| \( \rho \) (g/cm\(^3\))  | 7.891       |
| \( \Delta H_{\text{mix}} \) (kJ/mol) | -1.7785    |
| \( \Delta G \) (J/mol)     | -28976.76   |
| \( \Delta S_{\text{mix}} \) (J/K mol) | 14.90      |
| \( T_m \) (K)             | 1825.6      |
| \( \Omega \)              | 15.30       |
| \( \delta \) (%) atomic radius | 1.938      |
| \( \delta \) (%) WS radius | 2.6654     |
In Table 1, \( \rho \) corresponds to density, \( \Delta H_{\text{mix}} \) is mixing enthalpy, \( \Delta G \) the Gibbs free energy difference, \( \Delta S_{\text{mix}} \) the mixing entropy, \( T_m \) is the melting point, \( \Omega \) is the parameter for solid solution formation and \( \delta \) is the atomic size difference calculated in both covalent atomic radii and WS cell radius parameters. Calculating the \( \Delta H_{\text{mix}} \) and \( \delta \) parameters for a numerous HEA’s and metallic glasses, Guo and Liu [14] (see Fig. 1 in [14]) could delimitate the following regions in \( \Delta H_{\text{mix}} \) versus \( \delta \) diagram: HEA with a solid solution phase form when the three parameters are in the range of: \(-22 \leq \Delta H_{\text{mix}} \leq 7 \text{ kJ/mol, and } \delta < 8.5 \) and \( \Delta S_{\text{mix}} \leq 19.5 \text{ J/(K\cdot mol)} \).

In the case of VCrNiCoFeCu alloy the atomic-size difference \( \delta = 1.938 \) (in covalent atomic radius) the mixing enthalpy \( \Delta H_{\text{mix}} = -1.7785 \text{ kJ/mol} \) and \( \Delta S_{\text{mix}} = 14.90 \text{ J/(K\cdot mol)} \), respectively, as can be seen Table 1.

The values of \( \Omega \) and \( \delta \) for VCrNiCoFeCu match the criteria to form a solid solution.

### 3.2. Electrochemical properties and variation in the microstructure after the test

The open circuit potential (OCP) and polarization curves with electrochemical characteristic parameters of the investigated alloy in 3.5% sodium chlorite (NaCl) solution are shown in Fig. 1 and 2. The corrosion rates and electrochemical parameters of alloys in 3.5% NaCl solution are presented in Table 2 and 3. The corrosion potentials for induction melted sample are varying from \(-0.5489 \) to \(-0.6539 \text{ V SCE} \) and for the SPSed sample from \(-0.5846 \) to \(0.6921 \text{ V SCE} \) as can be seen in Tables 2 and 3.

Corrosion rate obtained from the electrochemical polarization measurements can be calculated by:

\[
\text{Corrosion rate (mm/y)} = \frac{3.27 \times 10^{-3} \times j_{\text{corr}} \times EW}{\rho}
\]

(6)

where \( j_{\text{corr}} \) (in \( \mu A/cm^2 \)) is the corrosion current density, EW the equivalent mass of the alloy, and \( \rho \) is the density of the alloy. EW is defined as follows [16],

\[
EW = \frac{1}{\sum \left( f_i n_i a_i \right)}
\]

(7)

where \( f_i, n_i, \) and \( a_i \) are mass fraction, electrons exchanged, and atomic mass, respectively, of the \( i \)th alloying element. The EW value of VCrNiCoFeCu is 31.157 and the corrosion rate (mm/y) as a function of the time can be found in Tables 2 and 3.
Table 2. Electrochemical parameters of the VCrNiCoFeCu alloy, prepared by induction melting method in 3.5% NaCl solution at room temperature (25°C).

| Time | $E_{corr}$ (V) | $j_{corr}$ (mA/cm$^2$) | CR (mm/year) | A (cm$^2$) |
|------|----------------|------------------------|--------------|------------|
| 0h   | -0.6539        | 3.2866                 | 0.042044244  | 0.2        |
| 1h   | -0.5776        | 3.5541                 | 0.045466272  |            |
| 3h   | -0.5871        | 3.2484                 | 0.04155566   |            |
| 5h   | -0.5489        | 3.2325                 | 0.041352163  |            |
| 24h  | -0.5585        | 3.3822                 | 0.043267219  |            |

Table 3. Electrochemical parameters of the VCrNiCoFeCu alloy, prepared by SPS method in 3.5% NaCl solution at room temperature (25°C).

| Time | $E_{corr}$ (V) | $j_{corr}$ (mA/cm$^2$) | CR (mm/year) | A (cm$^2$) |
|------|----------------|------------------------|--------------|------------|
| 0h   | -0.5846        | 3.435                  | 0.04394267   |            |
| 1h   | -0.6443        | 2.5612                 | 0.032764473  | 0.35       |
| 3h   | -0.6524        | 2.2113                 | 0.028288334  |            |
| 5h   | -0.6621        | 2.1964                 | 0.028097723  |            |
| 24h  | -0.6921        | 2.1051                 | 0.026929757  |            |

Figure 2. Polarization curves for SPS VCrNiCoFeCu alloy in 3.5% NaCl solution
For both alloys three specimens were tested to check the repeatability of the test results. Lower corrosion rate and higher breakdown voltage can be seen in the case of SPSed sample. The transient effect continues until the surface film thins to a degree that it becomes stable with respect to the environment. In the case of induction melted sample corrosion rates were almost stable during 24 h measurements. The differences in chemistry between these two alloys may influence the corrosion performance and this difference is regarded to the preparation methods. The achieved corrosion resistance of both HEA alloys can be regarded to a protective layer of chromium oxide that has evolved on the surface. In the case of induction-melted sample, this film so thin that it is even not visible by XRD, on the other hand the SEM-EDX demonstrated its presence, as can be seen Figures 5-6. The pitting corrosion resistance may be quantified using the passive breakdown potential, since sustained breakdown of the passive film is indicative of the onset of pitting corrosion. This can be seen after the passive regions from which current decreases rapidly with increasing potential. The significantly higher breakdown potential for this HEA designates greater protection against localized corrosion in the chloride-containing solutions, than that of the SS304 [8]. The spikes in current that are seen in Fig. 1. and Fig. 2 may be attributed to metastable pitting. These current fluctuations are caused by corrosion pits, which re-passivize ultimately.

3.3. Microstructure and phase constitution of VCrNiCoFeCu alloys

The XRD results for both alloys are shown on Figures 3-4. The results suggest that both the induction melted and SPS made HEAs are single-phase FCC alloys. It should be mentioned that the in the case of SPS method the sample was polluted by WC (tungsten carbide), which came from the milling jar. The XRD profile of SPS sample in Fig. 4. show significant phase of WC. The average lattice parameter was determined from the diffraction peak positions using the Nelson-Riley method [18]. The measured X-ray diffractograms indicated both samples have single-phase face-centered cubic (FCC) structure with lattice parameters of \( a = 0.3612 \pm 0.0002 \) nm and \( a = 0.3665 \pm 0.0002 \), for induction melted and SPSed samples, respectively.

![Figure 3. X-ray diffraction patterns of the induction melted VCrNiCoFeCu HEA](image-url)
The SEM micrographs of these alloys are shown in Figures 5-6. Microstructure also plays an important role in corrosion behaviour. Compositional differences which became from the mechanical alloying (the SPS sample was polluted by WC) may result in galvanic coupling, which can be much important than the effect of microstructure on general corrosion.

Figure 4. X-ray diffraction patterns of the SPS VCrNiCoFeCu HEA

Figure 5. SEM picture of induction melted VCrNiCoFeCu HEA before (a) and after (b) immersion test in 3.5% NaCl solution.
On the SEM figure of induction melted sample (Figure 5.) some chemical inhomogeneity can be seen before the corrosion test. After immersion a thin, high Cr containing film was formed as a protective coating for this alloy. On the Figure 6 one can see the SEM pictures for SPSed sample. The picture of ETD detector shows the surface morphology by secondary electrons. The brighter ones on the picture can be regarded to tungsten carbide pollution (from the milling jar). After the immersion these artefacts are removed, only a layer with high Cr content can be seen with some lower scale pitting corrosion.

4. Conclusions
The two samples of VCrNiCoFeCu prepared by induction melting and spark plasma sintering are crystallized in FCC structure. In the case of induction melted sample, high porosity can be observed. The phenomena can be regarded to Cu segregation effect, and to the fact, that due to their higher viscosity, HEAs tend to have higher porosity than conventional alloys (like steels).

As it can be seen in the Figure 5, a pitting corrosion is observable on the surface after immersion test in 3.5% NaCl solution (for 24 hours). This pitting corrosion behaviour can be attributed to galvanic action between dendrite and inter-dendrite compositions.

In the case of spark plasma sintered alloy, the dendrite like structure is not observable. This can be due to high WC contamination, what is inevitable in the case of mechanical milling.

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