Phase transformations in high-entropy FeNiCoCrAl alloys during oxidation

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Abstract: The evolution of phase composition and mechanical properties and the formation of oxide layers on Fe40−xNiCoCrAlx (x = 5 and 10 at.% ) alloys in long-term oxidation at 900 and 1000 °C were studied. In the initial cast state, depending on the aluminum content and valence electron concentration, the alloys contain only an fcc solid solution (VEC = 8 e/a) or a mixture of fcc and bcc phases (VEC = 7.75 e/a). Thin continuous oxide scales containing Cr2O3 and NiCr2O4 spinel formed on the surface of both alloys oxidized at 900 °C for 50 h. A further increase in the annealing time to 100 h leads to the formation of aluminum oxide Al2O3 in the scale on the Fe30Ni25Co15Cr20Al10 alloy, having high protective properties. An increase in the oxidation temperature to 1000 °C results in partial failure of the protective layer on the alloy with 10 at.% Al. Long-term holding at 900 °C (100 h) + 1000 °C (50 h) does not change the phase composition of the Fe35Ni25Co15Cr20Al5 alloy matrix, being indicative of its high thermal stability. In the two-phase Fe30Ni25Co15Cr20Al10 alloy, the quantitative ratio of solid solutions sharply changes: the amount of the bcc phase increases from 4 to 54 wt.% and its B2-type ordering is equiatomic or close ratio [1]. The HEAs are peculiar in that they possess low free energy and high mixing entropy has been of research focus recently. They contain more than four elements in an equiatomic or close ratio [1]. The HEAs are peculiar in that they form simple substitutional solid fcc or bcc solutions or a mixture of bcc + fcc solid solutions [2, 3]. Differently doped alloys in which simple bcc and fcc solid solutions form are among HEAs that have been studied most extensively. Numerous papers focus on the optimization of alloy structures and mechanical properties [4–8]. There are currently very limited data on the high-temperature oxidation resistance of these materials and the stability of their phase composition and mechanical properties in long-term high-temperature holding [9–14].

Our objective is to examine the effect of aluminum on the stability of phase composition, structure, and mechanical properties and on the formation of oxide layers in long-term temperature oxidation of the Fe40−xNiCoCrAlx alloys (x = 5 and 10 at.% Al) at 900 and 1000°C.

2. Experimental procedure

The Fe40−xNiCoCrAlx alloys (x = 5 and 10 at.% Al) were produced by arc melting in a high-purity argon atmosphere. The ingots were melted six to seven times to homogenize their composition. The starting components were high-purity materials (at least 99.98% purity).

The oxidation resistance of the alloys was examined in an electric arc furnace at 900 and 1000°C in air. The samples were periodically weighed in 5, 10, 25, 50, and 100 h. To measure the weight change of the samples, we used a Radwag precision balance (±0.0001 g). The oxidation resistance was assessed from the specific change in weight of the samples q (mg/cm²·h).

The phase composition of the starting alloys and those after high-temperature oxidation was analyzed with an Ultima IV diffractometer in monochromatic Cu-Kα radiation. The X-ray diffraction data were processed using the PowderCell 2.4 software for full-profile analysis of X-ray spectra for a mixture of polycrystalline phase components. The morphology and microstructure of scales on the starting and annealing alloys were examined with a Jeol Superprobe 733 scanning electron microscope and with a MIM-8 optical microscope. The mechanical properties were determined by automated indentation with a Berkovich pyramid under 3N load employing a Micron Gamma unit.

3. Results and discussion

The fcc solid-solution phase is known [15, 16] to form at elevated valence electron concentrations, VEC ≥ 8 e/a, in high-entropy alloys in most cases, while the bcc solid-solution phases are stable at VEC ≤ 6.87 e/a. If the valence electron concentration is 7.2 ≤ VEC ≤ 8 e/a, a mixture of two, bcc and fcc, solid solutions forms. According to our calculations, VEC = 8 e/a for the Fe35Ni25Co15Cr20Al5 alloy and 7.75 e/a for the Fe30Ni25Co15Cr20Al10 alloy (Table 1). Hence, the cast Fe35Ni25Co15Cr20Al5 alloy should contain only an fcc solid solution and the Fe30Ni25Co15Cr20Al10 alloy the bcc and fcc phases. X-ray diffraction data confirm the predicted phase composition of the alloys (Fig. 1 a, c). The Fe35Ni25Co15Cr20Al5 alloy is a single-phase solid solution with an fcc lattice with parameter a = 0.3571 nm and the Fe30Ni25Co15Cr20Al10 alloy is two-phase and contains bcc and fcc solid solutions. The fcc phase is predominant; its amount reaches 96 wt.% and that of the bcc phase is thus 4 wt.%.

The lattice parameter α of the bcc solid solution is 0.2862 nm and that of the fcc solid solution is 0.3603 nm (Table 1).

TABLE 1. Phase Constituents of the Cast Alloys, Lattice Parameters of the Phases, and Valence Electron Concentrations

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Phase constituents, wt.%</th>
<th>Lattice parameter, nm</th>
<th>VEC, e/a</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe35Ni25Co15Cr20Al5</td>
<td>100 FCC</td>
<td>0.3571</td>
<td>8</td>
</tr>
<tr>
<td>Fe30Ni25Co15Cr20Al10</td>
<td>96 FCC, 4 BCC</td>
<td>0.3603, 0.2862</td>
<td>7.75</td>
</tr>
</tbody>
</table>

Metallographic analysis of the high-entropy alloys in starting (cast) state showed that the Fe35Ni25Co15Cr20Al5 microstructure...
Fig. 1. X-ray diffraction patterns (a, c) and microstructures (b, d) for the Fe$_{30}$Ni$_{25}$Co$_{15}$Cr$_{20}$Al$_{10}$ alloy (a, b) and Fe$_{30}$Ni$_{25}$Co$_{15}$Cr$_{20}$Al$_{10}$ high-entropy alloys in starting state (SEM).

(Fig. 1b) included grains elongated in the crystallization direction and subgrains at grain boundaries and partially inside them. With higher aluminum content of the Fe$_{30}$Ni$_{25}$Co$_{15}$Cr$_{20}$Al$_{10}$ alloy, dendritic crystallization leading to light dendrites and a darker phase in the space between the dendrites was observed (Fig. 1d). A greater aluminum content of the alloy reduces VEC, in turn indicating that stability of the fcc solid solution reduces and the bcc phase forms through solid-phase decomposition mechanism.

Figure 2 shows variation in the specific weight of the samples $q$ (mg/cm$^2$) after oxidation of the Fe$_{35}$Ni$_{25}$Cr$_{20}$Co$_{15}$Al$_{10}$ and Fe$_{25}$Ni$_{35}$Cr$_{20}$Co$_{15}$Al$_{10}$ high-entropy alloys at 900°C for 100 h and then at 1000°C for 50 h. After short holding for 5 h at 900°C, the specific weight of the alloy samples increased differently. The alloy with 10 at.% Al oxidized much more slowly for the first 5 h than the alloy containing only 5 at.% Al.

Fig. 2. Variation in the specific weight of alloy samples after oxidation at 900°C (100 h) and further at 1000°C (50 h).

The specific weight of the Fe$_{35}$Ni$_{25}$Cr$_{20}$Co$_{15}$Al$_{10}$ alloy showed a stable gain for 30 h at 900°C and naturally increased further with longer holding as oxide film began to develop and grow. The Fe$_{25}$Ni$_{35}$Cr$_{20}$Co$_{15}$Al$_{10}$ alloy behaved differently. The sample significantly gained weight after the first 5 h and then partially lost its weight, which was accompanied by the formation of a thin brittle scale that spalled in some places. A dense scale formed further and oxidation proceeded not only without weight losses but also without weight gain, being indicative of high protective properties of the oxide film. However, a further increase of the oxidation temperature to 1000°C led to a sharp gain in the specific weight of the samples and growth of the scale thickness (Fig. 2).

The Fe$_{35}$Ni$_{25}$Cr$_{20}$Co$_{15}$Al$_{10}$ alloy showed a continuous increase in the specific weight within entire holding at 1000°C; $q$ was minimum for the first 5 h and the oxidation rate sharply increased in a period between 5 to 10 h. During the next exposure in the interval from 10 to 25 hours, a significant slowdown in the oxidation process is observed, and then there is a significant increase in the increase in the mass of the samples, this may indicate that the scale formed on the surface of the alloy does not have high protective properties at a given temperature. The situation was different for the Fe$_{35}$Ni$_{25}$Cr$_{20}$Co$_{15}$Al$_{10}$ alloy that contained more aluminum and less iron. After the first 5 h, the sample weight gain was much lower than that of the Fe$_{35}$Ni$_{25}$Cr$_{20}$Co$_{15}$Al$_{10}$ alloy. In a period between 5 and 10 h, $q$ substantially increased and then (10–25 h) the process sharply slowed down. In a period between 25 and 50 h, the curve showing variation in the specific weight changed its direction. When the sample cooled down, the scale partially spalled since the protective film failed under a cyclic change in temperatures because of different thermal expansion coefficients (TECs) of the scale and alloy matrix.

A two-phase oxide film containing Cr$_2$O$_3$ and NiCr$_2$O$_4$ spinel formed on both alloys at 900°C for 50 h. The scales were very thin (3–5 µm thick on the Fe$_{35}$Ni$_{25}$Cr$_{20}$Co$_{15}$Al$_{10}$ alloy and 7–8 µm thick on the Fe$_{35}$Ni$_{25}$Cr$_{20}$Co$_{15}$Al$_{10}$ alloy) and the X-ray diffraction patterns of both alloys had also reflections from the matrix phase of the fcc solid solution (Fig. 3).

Fig. 3. X-ray diffraction patterns for the Fe$_{35}$Ni$_{25}$Cr$_{20}$Co$_{15}$Al$_{10}$ alloy (a, b, e) and Fe$_{35}$Ni$_{25}$Cr$_{20}$Co$_{15}$Al$_{10}$ alloys after oxidation at 900°C for 50 (a, c) and 100 h (b, d) and after oxidation at 1000°C for 50 h (e, f).

The lattice parameter of the fcc solid solutions in the Fe$_{35}$Ni$_{25}$Cr$_{20}$Co$_{15}$Al$_{10}$ alloy was 0.3577 nm (since the near-surface metal layer was saturated with oxygen) and that in the Fe$_{35}$Ni$_{25}$Cr$_{20}$Co$_{15}$Al$_{10}$ alloy substantially decreased and became 0.3585 nm, indicating that...
metal ions diffused toward the oxidation front. Some diffusion processes occurred under the scale. For example, the aluminum diffusion rate increased with temperature. Hence, the aluminum concentration toward the metal surface became higher to promote the formation of Al₂O₃. In turn, this indicates that the fcc phase became depleted of aluminum and its lattice parameter decreased. The amount of the fcc phase in the 5 at.% Al alloy was 7 wt.% and that in the 10 at.% Al alloy was 41 wt.% This substantial difference can be attributed to varying thickness of the scales; as a result, X-rays penetrate to different depths of the sample. The main phase of the scales is presented by oxides of CrO₃ structure: their amount reaches 83 wt.% for Fe₃₅Ni₂₅Cr₂₀Co₁₅Al₁₀ and 42 wt.% for Fe₃₀Ni₂₀Cr₂₀Co₁₅Al₂₀. The amount of NiCr₂O₄ spinel in the scale of the Fe₃₅Ni₂₀Cr₂₀Co₁₅Al₂₀ alloy was 10 wt.% and that in the Fe₃₀Ni₂₀Cr₂₀Co₁₅Al₂₀ alloy was 17 wt%. Further holding changed the scale phase composition. The alloy with lower aluminum content had a scale after 100 h at 900°C containing two phases: Cr₃Fe₂O₅ and NiCr₂O₄ (Fig. 3b). The presence of Cr₃Fe₂O₅ can be explained by the fact that iron oxidized in long-term holding to form FeO that dissolved in Cr₂O₃ be explained by the fact that iron oxidized in long-term holding to form FeO that dissolved in Cr₂O₃ to create the Cr₃Fe₂O₅ phase with lattice parameters a = 0.4986 nm and c = 1.3646 nm, which is isosctructural to Cr₂O₃. The NiCr₂O₄ lattice parameter increased after oxidation at 900°C and became 0.8350 nm. In oxidation at 900°C for 100 h, Al₂O₃ formed on the Fe₃₀Ni₂₀Cr₂₀Co₁₅Al₁₀ alloy besides Cr₃Fe₂O₅. The X-ray diffraction pattern for the scale surface had no NiCr₂O₄ reflections since spinel separated from the scale surface after the thin continuous Al₂O₃ layer formed (being typical of the oxidation of Ni–Cr–Al alloys), so reflections from the fcc phase were predominant (Fig. 3d). After further oxidation at 1000°C for 50 h, the phase composition of the scales was similar to that of the oxide films after annealing for the same time at 900°C. In both cases, the X-ray diffraction patterns had reflections of NiCr₂O₄, Cr₂O₃, and fcc phase (Fig. 3e, f), but the amounts of phase constituents somewhat differed: the amount of Cr₂O₃ decreased and that of NiCr₂O₄ increased. This will further improve the high-temperature oxidation resistance of the alloys since diffusion processes slow down significantly in the layer with NiCr₂O₄. Cross-sectional studies of the Fe₃₀Ni₂₀Cr₂₀Co₁₅Al₁₀ alloy samples oxidized at 900°C + 1000°C revealed a wide continuous region of a light phase, identified by X-rays as the fcc solid solution, under the oxide film layer. This explains why there are no reflections of the bcc phase in the X-ray diffraction pattern. Hence, the surface layers are structured as follows: scale, fcc solid-solution region, and matrix with bcc + fcc phases. Since the papers [17–19] found differences in the phase composition of the FeNiCoCrAl alloys (in particular, for x = 5 and 10 at.% Al) after annealing at 900, 950, and 1100°C, we conducted additional X-ray diffraction and microstructural analyses of the samples’ end surfaces after complete grinding of the oxide layers to specify changes in the structure and phase composition of the alloy matrices (Fig. 4).

![Fig. 4. X-ray diffraction patterns for the Fe₃₅Ni₂₅Cr₂₀Co₁₅Al₁₀ (a) and Fe₃₀Ni₂₀Cr₂₀Co₁₅Al₁₀ (b) alloy matrices after annealing at 900°C (100 h) and 1000°C (50 h) and complete removal of the oxide layer](image)

After annealing at 900°C for 24 h, two phases were found to form in the FeNiCoCrAl alloy in [17]: fcc and B2-ordered bcc; at 1100°C, there was only fcc phase, the phase composition of the Fe₃₅Ni₂₀Cr₂₀Co₁₅Al₁₀ alloy remained unchanged after long-term high-temperature annealing in our case; there was only the fcc solid solution. This indicates that this alloy has high thermal stability since variations in line intensities in the X-ray diffraction pattern are not associated with structural changes but result from significant texture confirmed by the respective texture coefficient along the {200} crystallographic direction. For example, this coefficient τ was 0.2755 (300) after annealing for the alloy with 5 at.% Al and 0.2553 (200) for the alloy with 10 at.% Al (note that τ = 1 in the absence of texture) (Fig. 4a).

The phase composition of the Fe₃₀Ni₂₀Cr₂₀Co₁₅Al₁₀ alloy somewhat changed (Fig. 4b); the amount of the fcc solid solution sharply decreased from 96 to 46 wt.% and the B2-ordered bcc phase constituted 54 wt.%. Compared to the starting state, the lattice parameter of the fcc phase in the FeNiCoCrAl alloy increased from 0.3571 to 0.3586 nm and that of the FeNiCoCrAl alloy conversely decreased from 0.3603 to 0.3587 nm after long-term high-temperature annealing. The lattice parameter of the bcc solid solution increased to 0.2870 nm. These changes in lattice parameters occur because of diffusion-controlled redistribution of the alloy components (Table 2) among the phase constituents.

### TABLE 2. Phase Constituents and Lattice Parameters of Phases in the Alloy Matrix after Annealing at 900°C for 100h+1000°C for 50h

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Phase constituents</th>
<th>Phase content, %</th>
<th>Lattice parameter a, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₃₀Ni₂₀Cr₂₀Co₁₅Al₁₀</td>
<td>FCC</td>
<td>100</td>
<td>0.3586</td>
</tr>
<tr>
<td>Fe₃₀Ni₂₀Cr₂₀Co₁₅Al₁₀</td>
<td>FCC (B2)</td>
<td>46</td>
<td>0.3587</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.2870</td>
</tr>
</tbody>
</table>

Microstructural analysis of the annealed Fe₃₀Ni₂₀Cr₂₀Co₁₅Al₁₀ and Fe₃₀Ni₂₀Cr₂₀Co₁₅Al₁₀ alloy matrices by scanning electron microscopy (SEM) showed that long-term annealing substantially influenced their morphology. The alloy with 5 at.% Al became homogeneous after annealing, and thus the structure of even a preliminary etched sample was not practically revealed (Fig. 5a). The size of dendrites increased and their shape changed in the Fe₃₀Ni₂₀Cr₂₀Co₁₅Al₁₀ alloy, while a dark fine phase precipitated within light grains (Fig. 5b). The annealed alloy matrix and the distribution of elements in characteristic radiation were studied by SEM, which showed that the dendritic phase was enriched with chromium and iron, cobalt was distributed uniformly between the two phases, and nickel and aluminum were mainly in the space between dendrites and fine phase in the Fe₃₀Ni₂₀Cr₂₀Co₁₅Al₁₀ alloy.

![Fig. 5. Structure of the Fe₃₀Ni₂₀Cr₂₀Co₁₅Al₁₀ (a) and Fe₃₀Ni₂₀Cr₂₀Co₁₅Al₁₀ (b) alloy matrices after subsequent annealing at 900°C + 1000°C](image)

The mechanical characteristics of the alloys in cast state and after annealing were determined by automated indentation (Table 3).
After annealing, hardness of the Fe$_{32}$Ni$_{25}$Cr$_{20}$Co$_{20}$Al$_{5}$ alloy somewhat decreased to 1.8 GPa, which can be attributed to its high homogenization. The elastic modulus sharply reduced to 106 GPa since the lattice parameter of the fcc solid solution increased substantially, which in turn weakened interatomic forces and decreased $E$. The hardness increased to 3.1 GPa in the Fe$_{32}$Ni$_{25}$Cr$_{20}$Co$_{20}$Al$_{5}$ alloy as the B2-ordered bcc phase formed. This indicates that this alloy is a promising high-temperature oxidation-resistant material.

4. Conclusions

A series of studies focusing on the cast and annealed alloys in the Fe-50 at.%NiCoCrAlx system (x = 5 and 10 at.%) has established the following. In oxidation at 900$^\circ$C for 100 h, thin two-phase oxide films that contain NiCr$_2$O$_4$ spinel and Cr$_7$Fe$_2$O$_9$ oxide form on the Fe$_{32}$Ni$_{25}$Cr$_{20}$Co$_{20}$Al$_{5}$ alloy and Al$_2$O$_3$ and Cr$_7$Fe$_2$O$_9$ oxides on the Fe$_{32}$Ni$_{25}$Cr$_{20}$Co$_{20}$Al$_{5}$ alloy. Aluminum oxide in the scale promotes effective protection of the alloy against oxidation. However, when scale tempering temperature increases, Al$_2$O$_3$ separates and oxidation proceeds with the formation of NiCr$_2$O$_4$ and Cr$_7$Fe$_2$O$_9$ on the surface. A wide continuous region of the fcc solid solution under the scale on the Fe$_{32}$Ni$_{25}$Cr$_{20}$Co$_{20}$Al$_{5}$ alloy has been established to form for the first time. Long-term high-temperature annealing substantially changes the phase composition and mechanical characteristics of the Fe$_3$Ni$_{25}$Cr$_{20}$Co$_{20}$Al$_{5}$ alloy: the amount of the fcc solid solution sharply decreases to 46 wt.% and an ordered bcc (B2) phase forms. This substantially increases hardness: to 3.1 GPa. This indicates that the Fe$_{32}$Ni$_{25}$Cr$_{20}$Co$_{20}$Al$_{5}$ alloy is a high-temperature oxidation-resistant material.

5. References


9. T.M. Butler and M.L. Weaver, “Influence of annealing on the microstructures and oxidation behaviors of Al$_8$(CoCrFeNi)$_9$, Al$_{11}$(CoCrFeNi)$_{85}$, and Al$_3$(CoCrFeNi)$_{70}$ high-entropy alloys,” Metals, 6, No. 9, 222–233 (2016).


