Effect of solid-solution treatment on the microstructure and mechanical properties of high-nitrogen FeMnCrNiCo high entropy alloys

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Abstract. The effect of solid-solution treatment on the microstructure and tensile properties of high-nitrogen and nitrogen-free high entropy alloys (FeMnCrNiCo and FeMnCrNiCoN, N=0.36 mass.% and N=0.44 mass.%) has been investigated. It has been established that all materials under study possess an fcc crystal lattice, the lattice parameter of which increases with increasing nitrogen content. In comparison with the cast state, which is characterized by a coarse-grained dendritic microstructure, the alloys after solid-solution treatment show a more homogeneous microstructure. Solid-solution treatment does not significantly affect the mechanical characteristics of the alloys and their fracture micromechanisms.

1. Introduction

High entropy alloys (HEAs) form a new class of the multicomponent materials, which are rapidly gaining the attention of contemporary scientists. The study of HEAs began with the appearance of works introduced by Cantor et. al. [1] and Yeh et. al. [2]. HEAs typically consist of five or more components with atomic concentrations ranging from 5 to 35 at. % [3, 4]. Equiatomic alloys tend to form single-phase structures with face-centered cubic (fcc), body-centered cubic (bcc) and hexagonal close-packed (hcp) crystal lattices, and they possess some remarkable properties: corrosion resistance, high strength, ductility, and fracture toughness at room and cryogenic temperatures [1, 5]. Nevertheless, HEAs have low strength properties, which limit wide industrial applications of these materials [6, 7]. Nitrogen alloying can be used to improve strength properties of HEAs, like it was previously used for steels, because nitrogen is a strong austenite stabilizer, solid-solution strengtheners and is useful for enhancement of the pitting corrosion resistance of steels [8]. Currently, there are few works devoted to the study of nitrogen-bearing high-entropy or medium entropy alloys [9-11]. All of them show a positive effect of nitrogen-alloying on the strength properties of the HEAs even in the cast state [10-11].

In this study, we evaluated the influence of solid-solution treatment on the dendritic microstructure, tensile properties, and fracture micromechanisms in high-nitrogen and nitrogen-free high entropy alloys (FeMnCrNiCo and FeMnCrNiCoN, N=0.36 mass.% and N=0.44 mass. %).

2. Materials and methods

High entropy alloys with the chemical compositions Fe19.8Mn19.5Cr18.6Ni21.0Co21.1 (HEA, mass. %), Fe19.9Mn19.7Cr18.7Ni21.0Co20.3N0.36 (HEA-0.36%N) and Fe20.5Mn20.2Cr19.8Ni21.4Co18.5N0.44 (HEA-0.44%N) were obtained by vacuum induction melting in pure Ar atmosphere. Rectangular dumbbell-shaped specimens with the dimensions of the working part 12×2.6×1.4 mm (length×height×thickness) were cut...
by electrical discharge machining. Part of the specimens was examined in the cast state, the other part was subjected to conventional solid-solution treatment (SST) at a temperature of 1200 °C for 1 hour, followed by water-quenching. All specimens were mechanically grinded and electrochemically polished for final surface purification. The microstructure characterization was carried out using a light microscope (LM, Altami MET 1C). The X-ray diffraction (XRD) structural and phase analyses were done using a DRON 7 diffractometer in the 0-2θ Bragg-Brentano geometry with Co-Kα radiation. Microhardness measurements were performed using a Vickers hardness tester Duramin 5 (Struers) at a load of 1.96 N for 10 s. Tensile tests to failure were carried out at room temperature and an initial strain rate of $5 \times 10^{-4} \text{s}^{-1}$ using an electromechanical machine LFM-125 (Walter + Bai AG). The fracture surfaces were examined with a scanning electron microscope (SEM, Leo Evo, Zeiss).

3. Results and discussion

Typical LM micrographs of the alloys are presented in Figure 1. All investigated alloys have an inhomogeneous dendritic microstructure in the cast state (Figure 1 a, b, c), which is typical for HEAs [11]. Nitrogen alloying promotes partial homogenization of the cast microstructure, but this effect is insufficient. Areas of dendrites are enriched in Fe, Cr and Co, while interdendritic interlayers are characterized by increased contents of Mn and Ni atoms [11]. Conventional SST has a noticeable homogenizing effect but does not provide a fully homogenized microstructure without dendrites (Figure 1 d, e, f). The X-ray measurements testify that all investigated alloys possess a single-phase structure with an fcc crystal lattice. According to XRD analysis, no other phases have not been found both for cast and SSTed specimens. It was shown that nitrogen alloying with the concentrations of 0.36 mass.%N and 0.44 mass.%N is accompanied with an increase in the lattice parameter ($a$) relative to nitrogen-free HEA (Table 1). This behavior indicates the formation of a solid solution of nitrogen in the austenite phase. The comparison of the $a$-values for cast and SSTed specimens confirms an additional increase in nitrogen concentration in the HEA-0.44%N alloy after SST (Table 1). The latter testifies to the fact that in the cast HEA-0.44%N alloy nitrogen can form a small fraction of nitrides, which dissolve in SST.

![Figure 1. LM images of the microstructure of the alloys in the cast state (a, b, c) and after SST (d, e, f): (a, d) – HEA; (b, e) – HEA-0.36%N; (c, f) – HEA-0.44%N.](image)

Representative tensile stress-strain diagrams for the investigated alloys in the cast state and after SST are shown in Figure 2. Alloying with nitrogen significantly increases both the yield strength (YS) and the ultimate tensile stress (UTS) of the alloys and does not lead to a decrease in the elongation to failure $\delta$ (table 1). For cast alloys, the $\delta$-values for nitrogen-bearing specimens possess even higher values relative to a nitrogen-free alloy (Figure 2, table 1). After SST, the elongation of HEA noticeably
increased relative to the cast specimens due to partial dissolution of dendrites, and all alloys possessed similar plastic properties. The homogenization of the microstructure during SST assists an insufficient decrease in the strength properties of the alloys (YS, UTS, microhardness), however, no significant changes are observed between these properties of the cast and SSTed specimens.

![Tensile diagrams for cast (a) and SSTed (b) HEA, HEA-0.36%N, HEA-0.44%N.](image)

**Figure 2.** Tensile diagrams for cast (a) and SSTed (b) HEA, HEA-0.36%N, HEA-0.44%N.

**Table 1.** Mechanical properties and the lattice parameter of the austenitic phase (α) in the cast state and after solid-solution treatment of the alloys. YS – the yield strength, UTS – ultimate tensile stress, δ – elongation to failure, εu – a uniform elongation, Hμ – microhardness.

| Notation       | YS (MPa) | UTS (MPa) | δ (%) | εu (%) | Hμ (MPa) | a (Å) |
|----------------|----------|-----------|-------|--------|----------|-------|
| **Cast Specimens** |          |           |       |        |          |       |
| HEA            | 175      | 710       | 53    | 37     | 1785     | 3.593 |
| HEA-0.36%N     | 315      | 1075      | 65    | 41     | 2484     | 3.608 |
| HEA-0.44%N     | 370      | 1188      | 63    | 42     | 2603     | 3.609 |
| **Solid-Solution Treated Specimens** |         |           |       |        |          |       |
| HEA            | 170      | 714       | 63    | 38     | 1496     | 3.595 |
| HEA-0.36%N     | 300      | 1063      | 60    | 39     | 2438     | 3.607 |
| HEA-0.44%N     | 355      | 1195      | 64    | 41     | 2365     | 3.612 |

Figure 3 shows typical SEM images of the lateral and fracture surfaces of HEA and HEA-0.36%N specimens after tensile tests in the cast state and after SST (the characteristics of the HEA-0.44%N specimens are similar to those of the HEA-0.36%N specimens). The lateral surfaces of all the presented alloys are characterized by a pronounced deformation relief, which testifies considerable plastic deformation prior to the failure of the specimens. Slip traces and slip bands in several slip systems are observed in grain bodies. Microshear bands are clearly visible near the fracture zone, and microcracks are obviously formed inside of these bands (Figure 3). No grain boundary cracks were observed on the lateral surfaces of both nitrogen-free and nitrogen-alloyed alloys. Comparison of the deformation relief for N-free and N-bearing alloys shows that nitrogen-alloying stimulates planar slip (as it was previously confirmed in [10]) and inhibits wavy glide.

In the cast state and after SST, the initial HEAs are characterized by ductile transgranular fracture, numerous dimples are observed on the fracture surface (Figure 3 a, c). The mechanism of fracture of nitrogen-containing alloys remains ductile both in the cast state and after SST; however, the micromechanism of fracture is slightly transformed. The dominant fracture micromechanisms of the HEA-0.36%N alloy is dimple fracture, but along with dimples, some plain facets are visible (Figure 3 b, d). This is peculiar for alloys with a planar dislocation structure.
Figure 3. Typical SEM images of the lateral and fracture surfaces of specimens tensile tested in the cast state (a, b) and after SST (c, d): (a, c) – HEA; (b, d) – HEA-0.36%N.

4. Conclusion
The microstructure and mechanical properties of high entropy alloys FeMnCrNiCo and FeMnCrNiCoN (0.36 and 0.44 mass.% of N) have been investigated. Nitrogen-alloying is accompanied by solid-solution hardening of the alloys due to the dissolution of nitrogen in the fcc crystal lattice without detectable nitride formation. Solid-solution treatment promotes a more homogeneous microstructure relative to the cast specimens, but does not contribute to substantial variation in the mechanical properties of the alloys.

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