Microstructural Characterization and Optimization of CoCrCuFeMnNi High Entropy Alloy to be in Contact with Hydrogen

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Abstract: This study aims to develop a High Entropy Alloy (HEA) with reduced susceptibility to Hydrogen embrittlement (HE) and improved resistance to oxidation, potentially surpassing existing materials in hydrogen-rich environments.

Microstructural analysis revealed a dendritic structure where two FCC phases have been formed: a dendritic zone with the designed composition and a Cu-rich interdendritic structure with reduced Mn content. The second phase has been eliminated with the application of heat treatment but Cr-rich segregation in grain boundary appeared during a prolongated exposure at 1100℃, which could correspond to σ phase. Segregation of σ phase might be eliminated with an optimization of the composition or heat treatment conditions, achieving a single-phase solid solution.

Keywords: High Entropy Alloys; Hydrogen Embrittlement; Single-phase solid solution; Interdendritic structure

1 Introduction

The hydrogen industry is expanding rapidly to meet increasing energy demands, utilizing existing gas pipelines to transport hydrogen. However, current steels suffer irreversible damage from hydrogen exposure, known as Hydrogen Embrittlement (HE).

High Entropy Alloys (HEAs) are promising due to their excellent mechanical properties, even at cryogenic temperatures, making them suitable for hydrogen applications. The Cantor alloy, developed by B. Cantor [1], is a well-known HEA composed of five metallic elements in varying atomic percentages (5-35%) and a single-phase solid solution structure. This alloy exhibits improved ductility and strength resistance in hydrogen-rich environments [2]. Despite extensive research on HEA mechanical properties, there is limited information about their behavior concerning hydrogen damage.

This study focuses on modifying the Cantor alloy to enhance its performance when exposed to hydrogen. Mn affects oxidation behavior, leading to rapid oxide formation at high temperatures [3]. Some researchers have replaced all the Mn with Cu to create a more oxide-resistant material, resulting in a two-phase microstructure with a primary FCC structure enriched in Cu [3]. Given copper's low permeation [4] with respect to hydrogen, this work explores the possibility to develop an HEA variant that retains the beneficial properties of the original Cantor alloy while exhibiting improved resistance to hydrogen-induced damage and oxidation.

2 Experimental procedure

The CAPHAD method is employed to determine the target composition of the alloy optimizing the balance between Mn and Cu to achieve a composition window that results in a single-phase FCC solid solution.

Following multiple calculations using FactSage software and a steel database, a specific chemical composition has been determined that exhibits a single FCC phase window between 1000 and 1200 ℃. Quenching from a temperature within this range allows the retention of the FCC phase at room temperature.

The casting process to produce the HEA was conducted using an induction furnace under an argon atmosphere. Raw metals with a purity exceeding 99.5% were utilized to achieve a precise composition and clean alloy. The melt was poured into a stair-shape H13 metallic mold.

The microstructural characterization was done using a Field Emission Scanning Electron Microscope (SEM), while thermophysical properties were assessed using a Differential Scanning Calorimeter (DSC).

3 Result and discussion

All as-cast samples exhibit a dendritic structure. Two types of dendrites can be distinguished: primary solidified dendrites, which nucleate and grow first, and secondary solidified dendrites, which are finer and form between the primary ones. Samples from the thickest stair exhibit higher Secondary Dendrite Arm Spacing (SDAS) values compared to those from the thinnest stair.

In this material, two principal phases can be identified: FCC#1 and FCC#2. FCC#1 is a solid solution with the design, while FCC#2 is a Cu-rich phase.

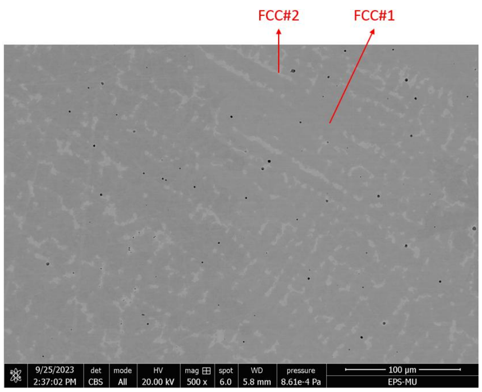

Figure 1 Disposition of FCC#1 and FCC#2 in the alloy

The results show a Cu-rich interdendritic structure. Moreover, the presence of Mn in interdendritic areas is evident but in a lower amount compared to Cu. From the equilibrium solidification diagram, it is known that the FCC#2 phase is the Cu-rich phase, and, taking into account the EDS results, the FCC#2 phase could be the second solidifying phase.

For the elimination of the FCC#2 and to obtain a single-phase FCC#1 solid solution, a heat treatment has been done: 900℃ for 24h + 1000℃ for 24h + 1100℃ for 72h and final quenching. The dendritic structure of the alloy disappeared where FCC#2 phase has been eliminated and FCC#1 solid solution was homogenized. However, due to the prolonged exposure at high temperature, Cr-rich grain boundary segregation appeared. This segregation probably corresponds to the σ phase as it is gathered by A.J. Maldonado [5] in Cantor alloy at a lower temperature. Additionally, it is proven that Cr segregation destabilize the FCC solid solution which could be stabilize or eliminate increasing Ni and Co [6] or optimizing the heat treatment procedure.

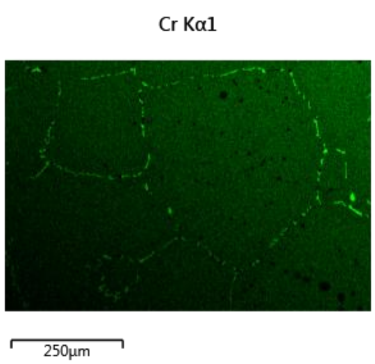

Figure 2 Cr-rich grain boundary segregation

4 Conclusion

The development of a CoCrCuFeMnNi high entropy alloy to be in contact with hydrogen has been done. The main results are the following:

- It is shown FCC#1 solid solution with a similar composition to the defined one, while FCC#2 is a Cu-rich phase.
- FCC#2 phase has been eliminated and FCC#1 solid solution has homogenized. However, a Cr-rich segregation appeared.
- Cr-rich segregation is associated to σ phase that could destabilize the FCC solid solution.
- The stabilization of FCC solid solution could be controlled increasing Ni and Co in the developed HEA or optimizing the heat treatment procedure.

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