Fabrication of 3D interconnected dual-phase heterostructures in CoCrFeMnNi high entropy alloy using the Liquid Metal Dealloying process with Cu melt

The dealloying reaction between a CoCrFeMnNi high-entropy alloy (HEA) precursor and molten Cu at 1095°C was investigated as a function of immersion time. EDX mapping and line analyses revealed that Mn and Ni, which have high reactivity with Cu, were the first to undergo dealloying reactions in the CoCrFeMnNi HEA precursor. Consequently, Cu-rich melt channels penetrated the precursor alloy, forming a unique 3D interconnected heterostructure.

There have been wide variety of developments for 3D interconnected materials using dealloying techniques. In general, dealloying is referred to a corrosion phenomenon in which the more active element is selectively removed from an alloy under certain environmental conditions. The liquid metal dealloying (LMD) process, which is different from chemical dealloying and vapor dealloying, has also been actively studied for a decade. In 2011, Wada et al. first reported this novel dealloying process to develop the 3D interconnected non-noble materials [1]. The LMD process is based on the miscibility relationship between the constituent elements of precursor alloy and a liquid metal [2-5]. Liquid metal is utilized as a dealloying medium, and it selectively takes out miscible elements from a precursor alloy. The selective dissolution results in interface diffusion of immiscible atoms, and the self-organization phenomenon of immiscible atoms into 3D interconnected morphology is involved. Simultaneously, the liquid melt penetrates the precursor material, and the 3D interconnected melt channels are formed due to the LMD reaction.

Previous LMD studies have focused on simple LMD systems where thermodynamic reactions can be easily predicted by miscibility relationships among elements of precursor alloy and metallic melt. However, this study aims to fabricate a new heterostructure microstructure by using a high-entropy alloy (HEA) composed of more than five principal elements as the precursor.

The CoCrFeMnNi HEA, known for its excellent mechanical properties at cryogenic temperatures, was homogenized at 1100 °C for 6 h, then cold-rolled with a 75% reduction and recrystallized at 1050 °C to prepare the precursor alloy. Holes were then machined into the specimens, and they were immersed in molten copper at 1095 °C for 2, 5, 10, and 12 min using a W wire.

The microstructure produced by LMD exhibited a complex 3D interconnected heterostructure, distinct from the typical dendritic cast structures or equiaxed recrystallized microstructures (Fig. 1). The thickness of the dealloyed reaction layer was measured at 228, 453, 766, and 708 μm for immersion times of 2, 5, 10, and 12 min, respectively. After 12 min of the LMD process, the entire specimen transformed into a 3D interconnected composite, indicating a significantly faster reaction rate compared to other metallic melts such as Mg.

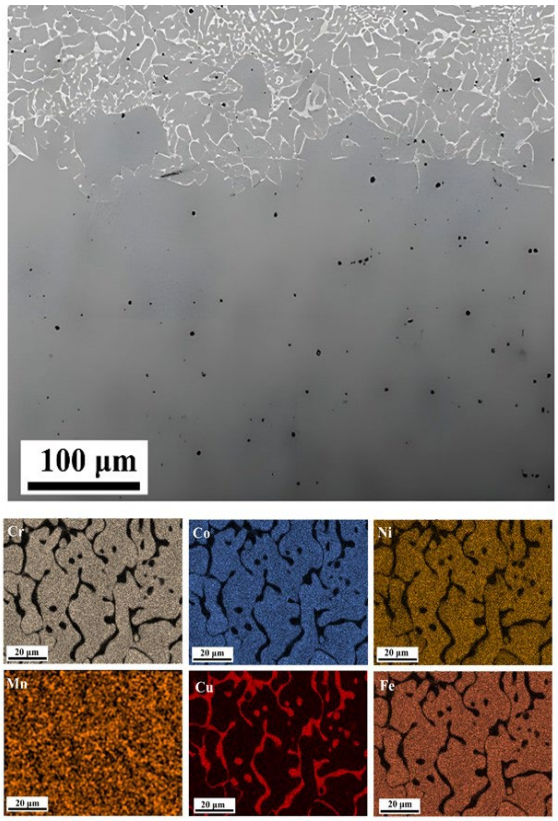

Fig. 1 Heterostructure developed by the LMD process using a CoCrFeMnNi precursor with Cu melt.

The fabricated heterostructure composite was formed by the self-organization phenomenon of the solid ligament phase and Cu-rich melt channels during the LMD process, as confirmed by EDS maps showing a 3D interconnected structure (Fig. 1). In the solid ligament phase, Cr, Co, and Fe were uniformly distributed, and a small amount of Cu (6.6 at.%) was also alloyed. In the Cu-rich melt channel region, Mn and Ni were dissolved around 5 at.% with small amounts of Cr, Co, and Fe also reacting and present in the melt channel. Based on the measured compositions, the mixing entropy was calculated, showing that the solid ligament phase exhibited a mixing entropy of 1.79R, characteristic of a HEA, while the Cu-rich melt phase exhibited a mixing entropy of 1.32R, indicating characteristics of a medium-entropy alloy.

To investigate the diffusion behavior and self-organization phenomena between the CoCrFeMnNi HEA precursor and Cu melt, a line EDS analysis was conducted (Fig. 2). The right graph shows that Mn and Ni were initially dissolved and detected in the Cu melt, with Mn being almost entirely dissolved and some Ni remaining in the solid ligament. Additionally, unlike previous LMD reactions where the melt's elements did not dissolve into the solid ligament, this study observed a significant amount of Cu alloying. This can be attributed to the high solubility of Mn and Ni in Cu despite their positive mixing enthalpy of 4 kJ/mol, as well as the tendency of Cu to dissolve in Co, Cr, and Fe at high temperatures, despite their high mixing enthalpy values.

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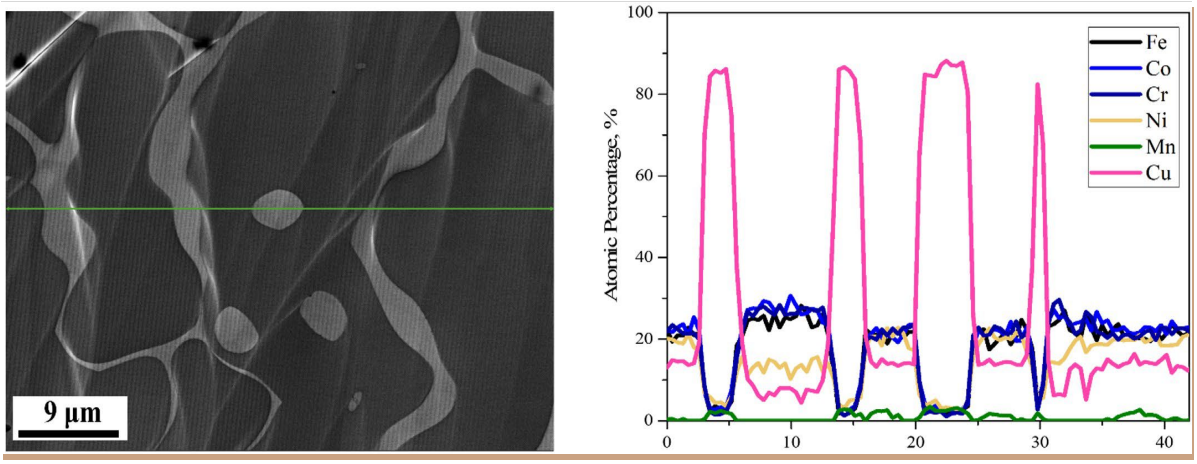

Fig. 2 Line EDX analysis results along the green line (left) crossing the solid ligament and Cu-rich melt phase regions.

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