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Paper Title: Microstructure, mechanical properties, and shape memory behavior of laser-directed energy deposited Co–20Fe–18Cr–19Mn high-entropy alloycomposites

Content :

Microstructural characterization and mechanical properties

The phase composition was analyzed using an X-ray diffractometer (XRD, Ultima IV, Japan). The microstructure and fracture surface of the samples, including the tensile specimens, were observed using OM (Axiolab 5, Carl Zeiss, Germany) and SEM (Mira 3, TESCAN, Czech Republic). The samples for OM observation were polished using alumina suspension and etched by Keller solution. Thermal analysis of the alloy was conducted using differential scanning calorimetry (DSC) in the temperature range of −50 to 500 °C at a rate of 20 °C

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min^{-1}.

The distribution of alloy elements was characterized using a field-emission electron probe microanalyzer (EPMA, JXA-8530, JEOL Ltd., Japan). The crystal structures of the L-DED alloy, heat-treated alloy, and those subjected to mechanical loading were compared using electron backscatter diffraction (EBSD, Aztec HKL, Oxford Inc., UK) at an accelerated voltage of 20 kV and step size of 0.7 μm.

As shown in Fig. 3(a), the tensile test and bending test follow the KS B0801 and ISO 7438 standards. To ensure the repeatability of testing, all sample conditions were tested at least ten times, and selected representative results. The tensile properties of the alloy were measured by a universal testing machine (UNITECH- T, R&B Inc., Republic of Korea) at a constant strain rate of 0.05

s^{-1}

. For the measurement of strain, the foil strain gauge with a gauge length of 2 mm was mounted cyanoacrylate adhesive strain gauge glue on the middle of the tensile test specimen, as shown in Fig. 3(c). Since the measurable strain limit of the foil strain gauge was 10 %, the strain larger than 8 % was estimated from the machine cross-head displacement. Vickers hardness measurements were conducted with a hardness testing

machine (HM-200, Mitutoyo, Japan). Ten indentations were made along the building direction with indentations being 0.5 mm apart from each other.

Fig. 4 illustrates the experimental procedure for evaluating the SME of the alloy. To assess the SME, the bending strains in the deformed specimens were calculated from the radii of curvature (=

$t/2r\times100$

, where

t

is the specimen thickness, and

r

is the radius of curvature) of 2 %, 4 %, and 6 %. Subsequently, the samples were subjected to an annealing heat treatment for 10 min for the shape recovery. Previous study on the casted shape memory alloy with the same chemical composition of this study showed that the HCP phase in the alloy can be fully transformed at the temperature of 600 °C [21]. On the other hand, as we will show later, the A_s and A_f temperatures of the DED printed alloy was higher than those observed for the casted alloy. For this reason, two different annealing temperatures of 600 and 700 °C were used for this study. The recovery strain of the alloys was calculated based on the radii of the annealing heat treated samples.

Mechanical properties

Fig. 12(a) shows the representative stress–strain curves of the L-DED and heat-treated HEAs. As shown in Table 1, an ultimate tensile strength of the HT samples was 743 ± 15 MPa, whereas the heat-treated HT samples showed an ultimate tensile strength of 849 ± 20 MPa. The results indicate that, after heat treatment, there was an improvement in the tensile strength of the samples. Moreover, the heat treatment effectively enhanced the elongation of the alloy, with an increase of more than double in both the HT and VT directions. Since the grain size was significantly increased during the heat treatment, this behavior cannot be explained by conventional Hall-Petch relationship. This enhancement was probably attributed to the phase transformation from an FCC-HCP dual-phase alloy structure to an FCC single-phase alloy structure during heat treatment. Compared to alloys with an HCP phase structure, FCC phase alloys exhibit better plasticity and deformation capability owing to relatively easy atomic slip during deformation. Thus, the alloy exhibited improved tensile elongation after heat treatment. On the other hand, segregated Mn near the molten pool boundaries was dissipated

during the heat treatment, which can compensate the loss in yield strength due to the grain growth by providing additional solid solutioning effect.

The stress-strain curves near the elastic loading regime from 0 to 0.4 % strain are shown in Fig. 12(b). In the elastic loading regime, it is interesting to note that some oscillations are present frequently regardless of the heat treatment. These oscillations are believed to be partly due to the complex residual stress state that was occurred in the L-DED process. Another possible reason for such oscillation was localized stress-induced phase transformation that can occur near the strain gauge length, which can induce local load shedding to the nearby region. From the non-oscillating curves, the elastic modulus of the alloy was estimated to be ~190 GPa, regardless of the heat treatment. Due to the oscillations, determinations of 0.2 % yield strength could not be made accurately. The yield strengths of the VT and HT samples in the as-printed condition were roughly estimated by 220 and 245 MPa, respectively, whereas the strengths after the heat treatments of the VT and HT samples were approximately 280 and 260 MPa, respectively.

The higher tensile performance in the HT direction compared with that in the VT direction is primarily attributed to the anisotropy introduced during L-DED process, which is a common occurrence in AM processes [23,30]. This anisotropy is primarily due to the columnar grains formed during the solidification process. These columnar grains typically exhibit higher grain boundary strength in the HT direction, which effectively hindering grain sliding and improve tensile properties. Conversely, a lower number of grain boundaries in the VT direction results in a relatively lower tensile performance [31].

Simultaneously, we conducted hardness tests on the alloy by performing numerous point measurements along the building direction before and after heat treatment. The results obtained by averaging the measurements indicated no significant differences in the hardness at various sampling points along the building direction. The average hardness of the alloy before heat treatment was 298 ± 20 HV, whereas the average hardness after heat treatment was 280 ± 22 HV. The primary reason for the reduced hardness after heat treatment is the increased grain size, which makes dislocations more prone to slip at the grain boundaries, thereby reducing the hardness. Another possible reason is the phase transformation of the alloy into an FCC single-phase structure after heat treatment. Because atomic slip in the HCP phase is relatively difficult compared to that in the FCC phase, the HCP phase structure contributes to higher hardness, leading to reduced hardness after heat treatment. In addition, the L-DED process generates a unique fine-grained cellular structure. The presence of finer grains can increase the macroscopic hardness because grain boundaries can impede the motion of dislocations during plastic deformation [32].

To study the SME of the alloy, we conducted bending tests on the as-printed and heat-treated samples deformed at 298 K followed by annealing at 600 and 700 °C. We found that there was no significant difference in the results of the annealing of the alloy at different temperatures. This is because, according to the analysis of the DSC curve, the alloy had already completed the reverse transformation at 423 °C, and higher temperatures did not yield different results. The as-printed samples did not exhibit an apparent SME, probably because their microstructure consisted of a near-full HCP structure, which does not have the capability to show shape memory behavior. However, for the heat-treated samples, the alloy exhibited a pronounced SME. As shown in Fig. 13(b), as the pre-strain increases, the pseudo-elastic strain of the alloy also increases. During the pseudo-elastic strain stage, the strain in the VB direction was slightly higher than that in the HB direction. Conversely, as shown in Fig. 13(c), as the pre-strain increases, the recovery strain decreases. The descent rate of the recovery strain in the HB direction is generally higher than that in the VB direction. The total recovery strain in Fig. 13(d) exhibits an increase with an increase in the pre-strain, with the VB direction strain rate being higher than that in the HB direction.

We posit that the alloy is in the austenitic stage, and that the application of external stress led to a phase transformation into the martensitic phase. With an increase in the pre-strain, more austenitic phases within the alloy were transformed into martensitic phases, enhancing the pseudo-elastic strain. Moreover, the amplified pre-strain causes shape memory alloys to store more strain energy during the pseudo-elastic strain stage, thereby reducing the remaining recoverable deformation in the recovery strain stage. Consequently, the recovery strain decreased with an increase in the pre-strain.

Sensitivity analysis of the conditions of pre-strain, annealing heat treatment temperature and sample orientation on the recovery strains were performed based on the linear regression method. Fig. 14 shows the sensitivity analysis results. Table 2, Table 3 show the values of R_2, Δ, F and P for pre-strain and temperature. The results show that, among the three experimental conditions of pre-strain, annealing temperature and sample direction, there are only meaningful correlations between pre-strain and the resulted recovery strains. In the pre-strain, the P-value is much less than 0.1, showing a clear correlation between the pre-strain and the experimental output results. This means that the shape recovery performance of the alloy is not significantly affected by the annealing temperature and sample direction. It shows a clear tendency of the ε_{pse} being increased and the ε_{rec} and ε_{tot} being decreased with increasing the pre-strain, with relatively significant determination coefficients of R_2 of around 0.7 for the ε_{pse} and ε_{rec}. It also shows that the annealing temperature has negligible effect on the recovery behavior with the slopes less than 0.001 %/°C (i.e. difference in recovery strain was less than 0.1 % for the two different annealing temperatures of 600 and 700 °C used in this study). The sample direction had a slight

effect only on the pseudo-elastic strain where the VB samples showed approximately 0.1 % higher pseudo-elastic strain than the HB samples.

Compared with the Cr-Mn-Fe-Co-Ni alloy prepared by L-DED process, the microhardness of the alloy in this study is higher in comparison with the reported values [33] (i.e. less than 265 HV). Regarding the tensile properties in comparison to the tensile properties of the L-DED processed Cr-Mn-Fe-Co-Ni alloy [15], the ultimate tensile strength of the alloy after heat treatment in this study is higher increased by approximately two times, with less elongations. The higher strength and the lower elongation of the studied alloy in comparison to the Cr-Mn-Fe-Co-Ni alloy seem to be due to the unique stress-induced FCC to HCP phase transformation.

In comparison with the previous reported shape memory alloys with martensitic transformation between FCC phase and HCP phase, the recovery strain of Co–20Fe–18Cr–19Mn shape memory alloy printed by L-DED process is higher than that of Co-Ni [[34], [35], [36]], Fe-Mn [37] and Fe-Mn-C [38] alloys (i.e. they all showed the total recovery strains less than 0.3 %). The $Cr_{20}Mn_{20}Fe_{20}Co_{35}Ni_5$ HEA prepared by casting process showed similar total recovery strain observed in this study [21]. The tensile yield strength of the casted $Cr_{20}Mn_{20}Fe_{20}Co_{35}Ni_5$ alloy was approximately 218 MPa, which was much lower than the strength of the HEA produced by the L-DED in this study. We attribute this phenomenon to the changes in finer austenite grain microstructure due to the rapid solidification occurred during the L-DED process in this study.