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TEM INVESTIGATION OF Cu-10Al-7Ag SHAPE MEMORY ALLOY IN AS-CAST STATE

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Abstract
Shape memory alloys (SMAs) are smart materials that exhibit thermoelastic martensitic transformations so that they can return to their original shape when heated or relieved. While NiTi is still the most commonly used SMA, copper-based SMAs have gained attention due to their cost-effectiveness and good functional properties. In this study, the as-cast microstructure of a Cu-10Al-7Ag SMA alloy is investigated by transmission electron microscopy (TEM). The addition of silver as a microalloying element is of particular interest due to its limited solubility in the β-phase and its potential influence on phase stability and transformation behavior. TEM analysis revealed the presence of fine martensitic structures and potential nanoscale precipitates that could play a role in transformation temperatures and mechanical behavior. The analyzes confirmed the presence of martensitic structures; mainly the 18R (β_1') martensite phase. The results are discussed in the context of phase evolution from the high-temperature β phase and the influence of Ag on the suppression of eutectoid decomposition and the improvement of microstructural refinement. These findings provide valuable contributions to optimize the composition of Cu-based SMAs for improved functional performance.

***Keywords**: Shape memory alloy, Cu-Al-Ag alloy, TEM analysis, martensitic transformation, microstructure*

1. INTRODUCTION

Shape memory alloys (SMAs) are a class of functional materials that can recover large, apparently plastic strains through a reversible, diffusionless martensitic transformation [1-3]. NiTi continues to dominate among commercially relevant systems; however, copper–based SMAs have gained renewed attention as they combine low raw material cost with high electrical/thermal conductivity, ease of casting and welding, and broad tunability of transformation temperatures [1-5]. In Cu-Al alloys, thermoelastic β → martensite transformation is responsible for both the one-way and two-way shape memory effects as well as superelasticity. The crystal structure of martensite can adopt several long-period stacking variants (2H, 18R, 6R, etc.), the selection of which is sensitively controlled by the Al content, the alloying additions and the cooling rate [1,4,5]. Recent calorimetric and in-situ diffraction studies suggest that Ag can retard long-range ordering ($A2 \rightarrow B2 \rightarrow L2_1$) during cooling, broadening the β-phase field and facilitating the formation of modulated 18R martensite instead of eutectoid equilibrium products [1-5].

Despite these advantages, systematic electron microscopic investigations of Cu-Al-Ag alloys are still not so well studied. Most reports focus on the bulk thermomechanical behaviour or on Ag-free Cu-Al-Mn and Cu-Al-Ni counterpart alloy systems [1-5]. This TEM investigation is based on the as-cast nano-surface of the Cu-10Al-7Ag alloy. Using bright field/dark field imaging, electron diffraction (SAED) and nanometre-scale energy dispersive X-ray spectroscopy (EDS), we (i) identify the predominant martensitic variant (18R/β_1'), (ii) reveal a sub-100 nm precipitate

population with increased Ag content and (iii) correlate these features with the solidification pathway, which can be deduced from phase diagrams.

2. EXPERIMENTAL

The Cu-10Al-7Ag shape memory alloy was prepared by melting high-purity raw materials: copper (99.9%), aluminum (99.5%), and silver (99.99%) supplied by Mateck Material-Technologie & Kristalle (Jülich, Germany). Melting was carried out in an electric-arc furnace that was vacuumed and purged multiple times with argon to reduce oxidation. The alloy was remelted more than four times to ensure chemical homogeneity and then cast into cylindrical molds measuring 8 × 12 mm. For metallographic preparation, samples were sectioned and mechanically ground using silicon carbide abrasive papers with grit sizes of 320#, 600#, 800#, 1200#, and 2400#. Final polishing was performed using 1 μm and ≤0.2 μm diamond paste on automated polishing systems (Citopress-20 and Tegramin-30, Struers, Willich, Germany).

Transmission electron microscopy (TEM) investigations were conducted using lamellae prepared by focused ion beam (FIB) milling with a Helios 650HP SEM/FIB dual beam system (Thermo Fisher, USA), equipped with an Octane Pro EDS detector (EDAX Inc.). TEM imaging utilized two advanced microscopes: a Tecnai G2 F20 operating at 200 kV with energy dispersive X-ray microanalysis (EDX), HAADF detector for STEM imaging, and high-resolution Gatan UltraScan and SIS Megaview cameras; and a Titan 80–300 S/TEM microscope operated at 300 kV with spherical aberration correctors for both probe and imaging optics. TEM modes included bright field, dark field, selected area electron diffraction (SAED), and high-angle annular dark field (HAADF), applied to lamellae approximately 10 × 8 μm in size.

3. RESULTS AND DISCUSSION

Figure 1. shows the bright field (BF) and dark field (DF) images as well as the diffraction pattern of the selected area (SADP) of the as-cast sample. The images clearly show martensite plates with a width of 150 to 800 nm, which were identified as the 18R phase. The SADP corresponds exactly to the [010] zone axis of the R18 martensite and exhibits a very slight monoclinic distortion with $\beta = 89.7°$. This diffraction pattern exhibits a contrast with a periodicity of 0.619 nm, which is characteristic of the 18R stacking sequence visible in the DF image of the (0012) spot. The streaks observed between the stacking patches likely result from numerous structural defects within the martensite variants, probably caused by internal stresses.

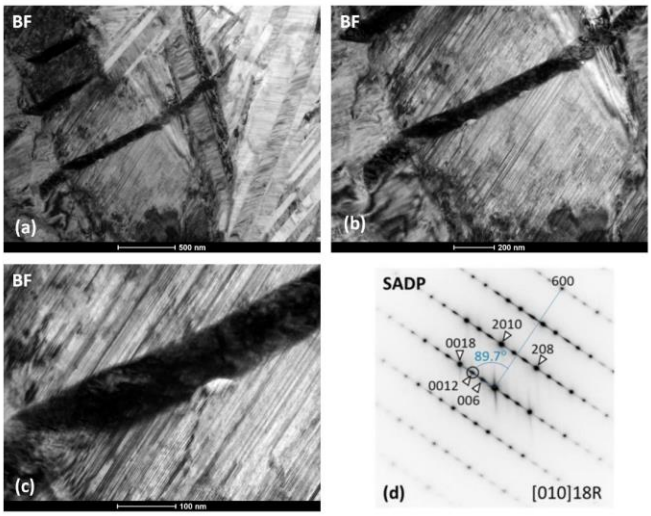

Figure 1. TEM images of the Cu-10Al-7Ag SMA alloy in cast condition: (a) bright-field TEM image taken at higher magnification and (b) dark field TEM image revealing 18R stacking sequence, (c) bright field TEM image taken at low magnification and corresponding (d) dark-selected area diffraction pattern (SADP).

A STEM analysis was carried out to determine the distribution of the most important alloying elements. Figure 2 shows the STEM-HAADF image together with the corresponding element distribution maps. It can be seen that the elemental maps show a random, highlighted area, an Ag precipitate within the as-cast Cu-Al matrix, with the image highlighting that the alloy matrix contains high concentrations of Cu and Al. The length of these precipitates ranges from approximately 0.5 microns to several microns.

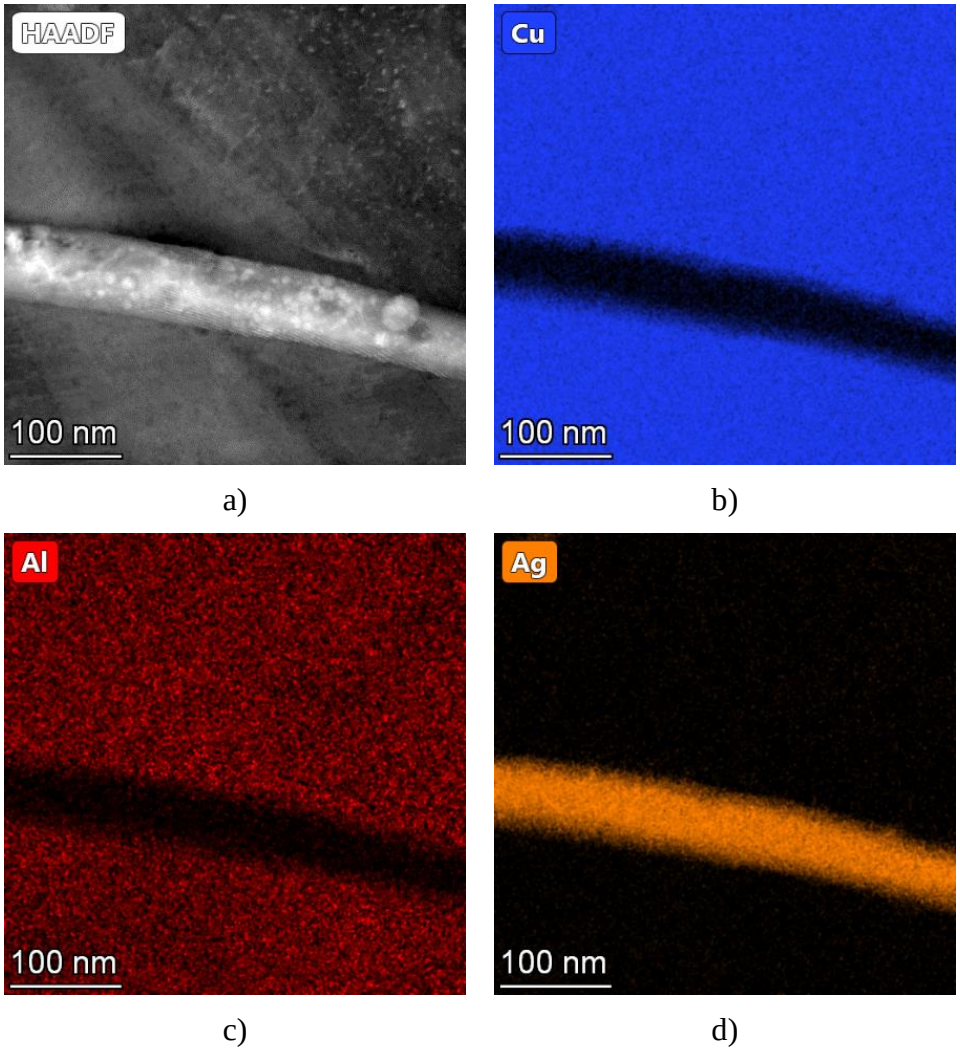

Figure 2. STEM HAADF and EDS elemental maps of the Cu-10Al-7Ag SMA alloy in as-cast condition (a) STEM-HAADF image, (b) Cu element distribution map, (c) Al element distribution map, (d) Ag element distribution map.

Figure 3. shows the results of the quantitative chemical analysis carried out for the indicated areas and indicates the composition of the three microstructural constituents observed in the as-cast sample. It can be seen that the general composition of the as-cast sample (matrix plus Ag precipitates) differs slightly from the nominal composition. The measured composition is depleted in both Al and Ag, which is most likely due to the high heterogeneity of the as-cast sample. This heterogeneity may be mainly related to the different density of Ag precipitates in the microstructure, as they also contain a considerable amount of Cu and a small amount of Al, as can be seen in Figure 3.

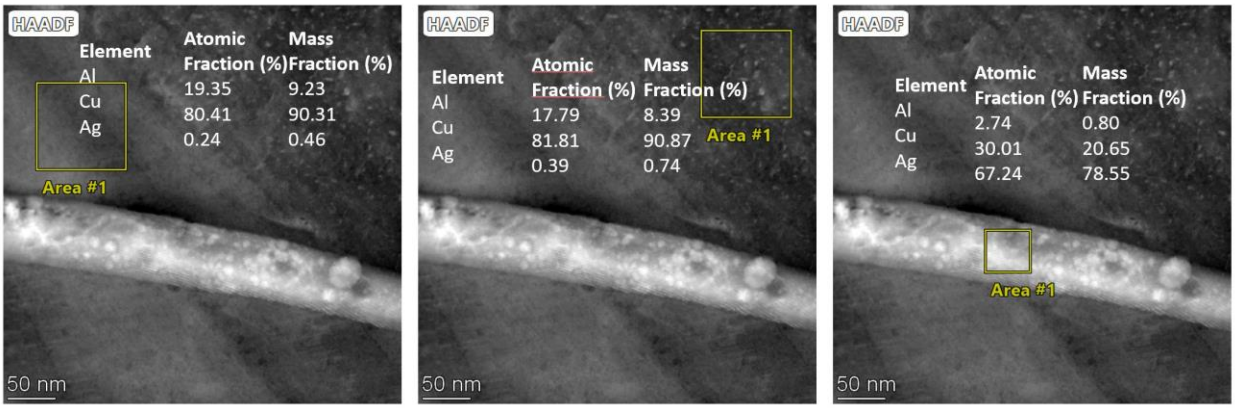

Figure 3. STEM HAADF and results of chemical analyses performed in the indicated areas of the Cu-10Al-7Ag SMA alloy in as-cast condition.

4. CONCLUSION

The Cu-10Al-7Ag shape memory alloy was successfully melted by vacuum electric-arc furnace by several remelting cycles to ensure chemical homogeneity. TEM analysis revealed the presence of martensitic plates with a width of 150 to 800 nm, which were identified as the 18R phase. This was confirmed by diffraction patterns in selected areas showing a characteristic 18R stacking periodicity and a slight monoclinic distortion. STEM-HAADF imaging and elemental mapping showed a largely random distribution of Ag precipitates in the as-cast Cu-Al matrix, with precipitate lengths ranging from about 0.5 to several microns. Quantitative chemical analysis indicated slight deviations from the nominal composition, in particular a depletion of Al and Ag, which was attributed to microstructural heterogeneity caused primarily by the different density of Ag precipitates with Cu and low Al contents. Overall, these results provide valuable insights into the microstructural properties and chemical distribution within the as-cast Cu-10Al-7Ag alloy, which are essential for understanding its shape memory behaviour and guiding future alloy design and processing.

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