Alloys and Intermetallics

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Microstructure evolution in annealed $Co_{38}Ni_{33}Al_{29}$ shape memory alloy

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Alloys in the Co-Ni-Al system and even their shape memory properties have been studied for decades as the cobalt-based alloys were supposed to have higher transformation stresses and wider intervals of superelasticity than other shape memory alloys (SMA). As these alloys are ferromagnetic the magnetic shape memory effect could be expected like in Ni-Mn-Ga and similar alloys. Nevertheless, the published data are controversial as alloy preparation and its thermomechanical treatment are complicated and the state of the material is very sensitive to slight changes in thermomechanical history [1]. Additionally, the two-phase structure in the high-temperature austenitic state is an exception within the SMA. It contains a B2 ordered (Co,Ni)Al matrix and A1 fcc solid solution particles. The A1 (interdendritic) particles remain untransformed, whereas the B2 matrix transforms martensitically into the $L1_0$ martensite [2]. Only non-modulated $L1_0$ martensite was observed in Co-Ni-Al based alloys.

Using the Bridgman method, a set of unidirectional solidified / single crystalline samples was prepared. The samples were investigated using different microscopic methods including LOM, SEM+FIB (including EDS and EBSD), TEM, SPM (as AFM and MFM) and other methods as ultrasound wave propagation and mechanical testing. This wide set of used methods gives a complex view on a rather uncommon behaviour of these ferromagnetic SMA.

It was found that martensite observed at room or even higher temperature is not the thermodynamically stable one, but rather stress induced. The equilibrium martensitic transformation is observed close to 200 K by both in-situ neutron scattering and magnetic susceptibility measurements. The stress induced martensite existing above its equilibrium temperature has the same structure as the equilibrium one. Its appearance is given by pronounced premartensitic phenomena, which can be observed in a wide temperature region. This region shall be connected with the region of superelastic behaviour, which was observed.

There exists a large difference between “as grown” and “annealed and quenched” samples. While the first group shows simple elastic behaviour, the second exhibits significant superelasticity with strong orientation dependence. The explanation must be connected with established high temperature equilibrium during annealing and the processes of its relaxation after quenching. The set of various precipitates was already observed in quenched samples: In addition to the major constituents (B2-type ordered matrix and A1 fcc particles), fcc cobalt solid solution precipitates ranging from 5 to 25 nm were observed in material grown with pulling rate 28 $mm\cdot h^{-1}$ and annealed at 1548 K/4 h [3]. The microstructure of an annealed (1548 K/4 h, pulling rate 38 $mm\cdot h^{-1}$) alloy was investigated by TEM and rod-like precipitates of hcp-Co 10–60 nm long were observed in the austenite phase. The orientation relationship between the precipitates and the B2 matrix was found to be the Burgers orientation relation. The martensite crystal structure is tetragonal $L1_0$ with a (1–11) twinning plane [4]. Many micron-sized non-twinned, single and triple $\{111\}_{B2}$ twinned precipitates with partial $L1_2$ ordering were observed in the austenite matrix, besides the interdendritic A1 phase in material grown with pulling rate 104 $mm\cdot h^{-1}$ and annealed 1373 K/72 h [5]. The orientation relationship between precipitates and matrix in such sample was determined to be the Kurdjumov-Sachs orientation relationship. STEM-EDX analysis indicates that twinned and non-twinned precipitates are Co-rich and Al- and Ni-deficient with respect to the matrix and with a lower Co/Al ratio for the latter, a difference possibly related with the site of precipitation with respect to the eutectic regions. A 3D morphology investigation of precipitates with FIB/SEM slice-and-view imaging revealed that the single $\{111\}_{B2}$ twinned precipitates have a plate-like shape with flat {111} faces while the non-twinned precipitates have a lath-like shape and can be curved.

Besides the precipitation in the matrix the annealing causes dissolving of interdendritic particles. Such process enriches the matrix with cobalt atoms and leads to concentration gradients on the particles' borders.

In the sample, grown with a pulling rate of 104 mm·h^{-1} and annealed at 1623K/1h, the matrix shows large martensite regions while interdendritic precipitates have a complicated structure with enclosed B2 austenite areas. Also, a precipitate-austenite-martensite sandwich structure with residual austenite of several hundred nanometres wide is formed due to the depletion of Co and enrichment of Al in the chemical gradient zone and the strong martensitic start temperature dependency of the element concentrations. The austenite $[100]_a$ direction is found to be parallel to the martensite $[110]_m$ direction in this case, confirming the origin of the sandwiched area as retained austenite, Fig. 1. The mentioned processes in microstructure and ordering of $Co_{38}Ni_{33}Al_{29}$ alloy will be discussed and related to elastic properties evolution.

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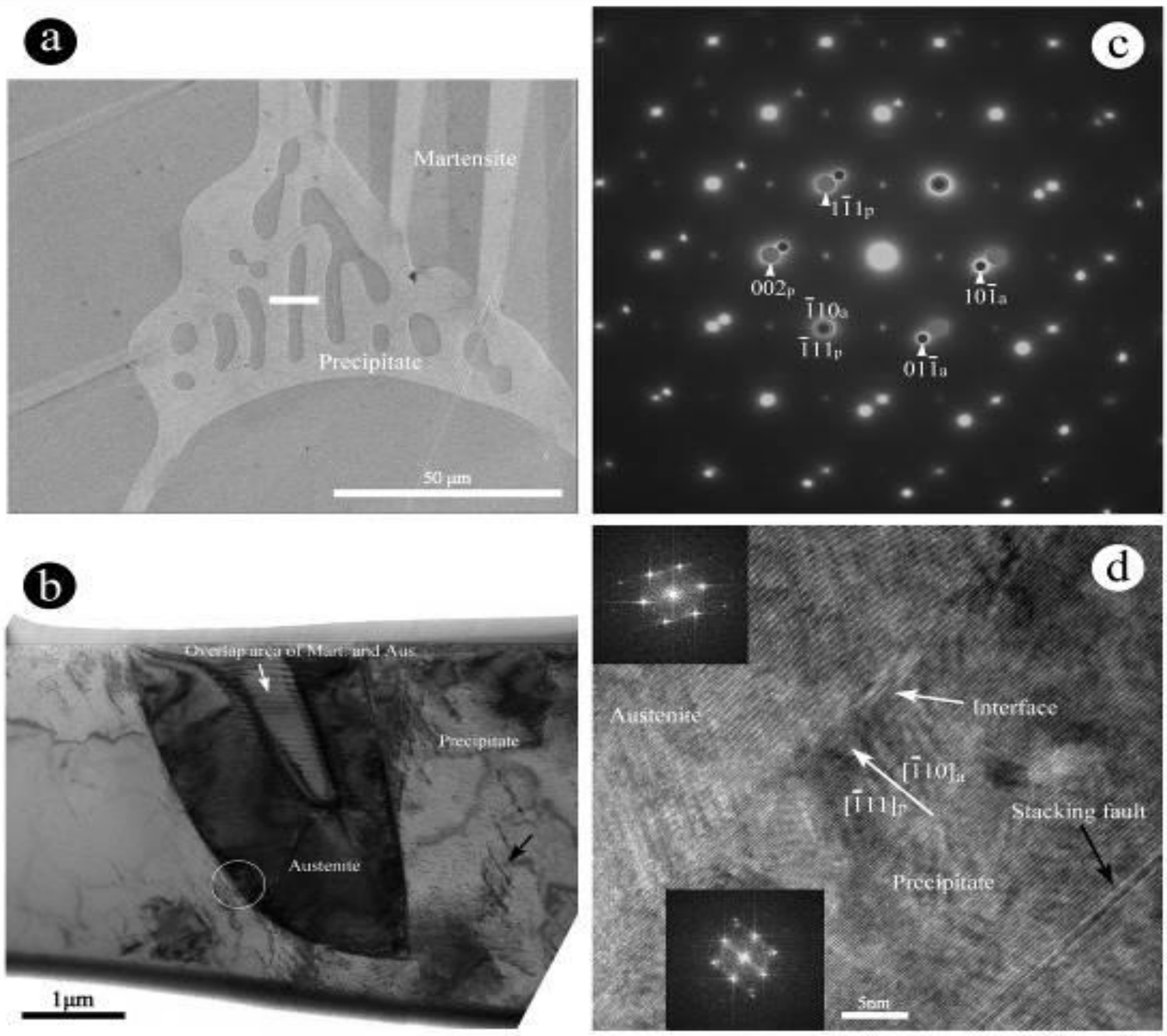

Figure 1. (a) SEM image sample grown with a pulling rate of 104 mm·h^{-1} and annealed at 1623K/1h, which shows the interdendritic morphology of a precipitate (white bar indicates the position where the TEM lamella was prepared by FIB), (b) BF TEM image of the FIB lamella, (c) Electron diffraction pattern taken from the area indicated by the white circle in (b) ($[111]_a$ / $[110]_p$), (d) HRTEM image of the interface of the precipitate and austenite corresponding to (c) including some FFT patterns.