Study of the transitory formation of α_1 bainite, as a precursor of α-phase in tempered SMAs

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ABSTRACT

Bainite transitory formation, during the heating of a martensitic copper base SMA, was predicted by DSC and DTA and confirmed by XRD, OM and TEM only in hot pressed air cooled state homogenized and tempered at 573 K. In this heat treatment state, due to the pre-existence of α-phase, bainite amount is expected to be too low, therefore non-distinguishable, for higher tempering temperatures, where it is suggested that transitory α_1 bainite turned to equilibrium α-phase. The results suggest that bainite formation could be considered as a precursor of α-phase during the heating of Cu-Zn-Al martensitic alloys, with no pre-existing α.

Keywords: Cu-Zn-Al shape memory alloys, martensite, α_1 - bainite, α- phase, transitory phenomena

1. INTRODUCTION

The discovery of bainite by Davenport and Bain, in 1930, enabled the development of modern bainitic alloys such as transformation induced plasticity (TRIP)-assisted steels which can reach yield strength above 600 MPa and tensile strength above 1000 MPa [1]. In contrast to martensite transformation, which is of shear-type (diffusionless), bainite transformation is of diffusion-controlled type because no intermediate, transition lattice was observed even in the very tip of the bainite plate [2]. After several decades of intensive fundamental research of bainite transformation in steels, various issues are still not fully understood such as bainite formation from plastically deformed austenite and its large growth rate and autocatalytic nucleation [3]. Considering the increasing importance of fundamental research of bainite transformation, distinctive sections have been assigned to this phenomenon within International Conferences on Martensitic Transformations (ICOMAT) even since 1986 as well as special issues of some cutting edge journals such as Scripta Materialia [4]. Moreover, as an effect of extending the presence of martensite transformation in various other materials, beside ferrous alloys [5], bainite transformation was also reported in nonferrous materials such as Shape Memory Alloys (SMAs) the governing mechanism of which relays on stress-induced reorientation of martensite plate variants and their reversion to austenite on heating [6]. Thus, during isothermal ageing of martensitic Cu-Zn-Al SMAs in the range 453-573 K, the formation of transitory α_1 bainite (9R orthorhombic) was reported that became disordered (3R) and finally transformed into equilibrium α-phase [7]. In the case of a Cu-21.6 Zn-7 Al (mass. %) SMA, stable bainite was observed only after homogenization and tempering at 573 K while in other heat treatment states bainite was considered as a precursor of equilibrium α-phase formation during the heating of martensitic alloys [8].

The present paper aims to bring more evidence of the presence of bainite in a Cu-21.6 Zn-7 Al (mass. %) SMA after homogenization at 1073 K and tempering at 573 K.

2. METHODOLOGY

After casting, hot pressing (1023 K/ air) and homogenization (1073 K/ 18 ksec/ water), some of the specimens of a Cu-21.6 Zn-7 Al (mass. %) SMA were tempered (573K/ 300 sec/ water). The specimens were prepared, for differential scanning calorimetry (DSC), differential thermal analysis (DTA), X-ray diffraction (XRD), as well as optical microscopy (OM) and transmission electron microscopy (TEM) studies, as previously described [8].

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DSC measurements were done on a 2920 Modulated DSC TA INSTRUMENTS unit, with a heating rate of 10 K/min. DTA experiments were performed on a MOM Q-01500D derivatograph with a heating rate of 5 K/min. XRD tests were carried out on a JEOL JDX-3500 diffractometer with CuK_α radiation, on $2 \theta = 40 - 80^0$. OM observations were performed on a LEICA optical line with Aristomet light microscope and Orthomat E exponometer. TEM observations were made with a JEM 2000FX transmission electron microscope operating at 200kV, with double tilt sample holder.

3. RESULTS AND DISCUSSION

3.1 DSC and DTA thermograms

In order to emphasize the transformations occurring during the heating of homogenized Cu-21.6 Zn-7 Al (mass. %) SMA two typical thermograms, recorded by calorimetric and thermal analysis techniques, are shown in Fig.1
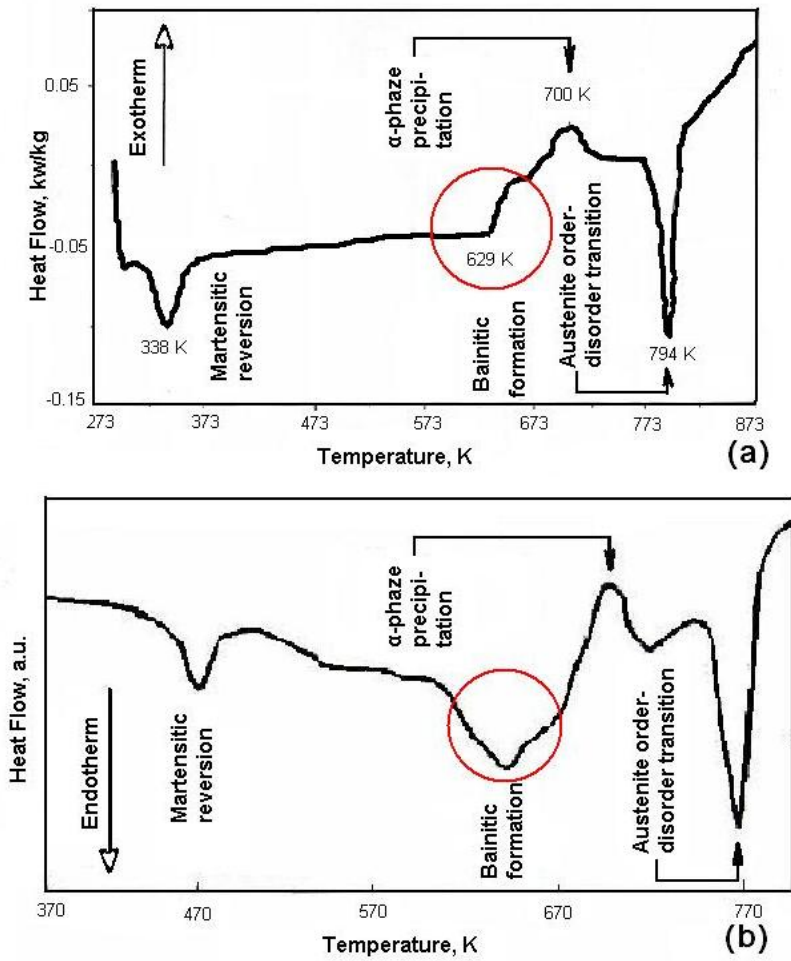

Fig. 1 Thermograms recorded by two thermal analysis techniques, during the heating of homogenized (1073 K/ 18 ksec/ water) Cu-21.6 Zn-7 Al (mass. %) SMA: (a) DSC chart; (b) DTA chart.

On both DSC and DTA charts, from Figs. 1(a) and (b), respectively, three solid state transformations were identified. Considering that the specimen is in martensitic state, as an effect of water-quenching, the first endothermic peak would correspond to reverse martensitic transformation, the exothermic peak would represent α-phase precipitation and the second endothermic peak would reveal an order-disorder transition of austenite [9]. In addition, it is presumed that the flat endothermic peak, located above 600 K, corresponds to bainite formation, which occurs between approx. 535 and 651 K. This suggests that bainite transformation can be triggered in the specimens tempered at 573 K being favored by isothermal holding. By means of DSC charts, the specific enthalpy absorption corresponding to bainite formation was determined as approx. 14 kJ/ kg.

The two thermograms from Fig. 1 have similar aspects and locations of the three high-temperature transformations. However, even if this detail is unimportant for the present discussion, they reveal different locations for reverse martensitic transformation: around 330 K on DSC chart and around 470 K on DTA chart. This could be an effect of the difference between heating rates, since DTA heating was performed with 5 K/ min which is half of DSC heating rate. Since reverse martensitic transformation is favored by high temperature-variation rates, this could be the reason why this reaction was retarded and occurred at higher temperatures on DTA chart. The presumed peaks of transitory bainite formation look different on DTA and DSC charts: more prominent on DTA and flatter on DSC but this could be another effect of different heating rates, as well.

3.2 XRD patterns

The calculated values of Miller indices, interplanar spacings and 2θ angles, as well as measured values of 2θ, in the significance region $40 - 80^0$, have been summarized in Table 1. The phase under evaluation have been β_2 austenite (B2, a=0.294 nm) [10], β_2' martensite (M9R monoclinic, a=0.441 nm; b=0.268 nm, c=1.92 nm and β=88.4^0) [11], α_1 bainite (9R orthorhombic, a=0.452 nm; b=0.264 nm and c=1.918 nm) [12] and α-phase (face center cubic, fcc, a=0.375 nm) [10].

Table 1. Calculated and experimental parameters used for indexing the diffraction peaks

No	Phase	Calculated values (hkl)	d_{hkl}, nm	$2\theta,^0$	Experimental values of $2\theta,^0$
1	β_2'	$(1\bar{1}\bar{1})$	0.2531	40.48	42.01
2	β_2	(110)	0.2358	43.58	44.02
3	β_2'	(200)	0.2293	44.88	45.48
4	α_1	$(\bar{1}\bar{1}3)$	0.2146	48.16	48.06
5	β_2'	$(0\bar{1}\bar{6})$	0.2058	51.56	52.17
6	β_2'	$(2\bar{1}6)$	0.1518	72.19	72.90

Tempering effects are revealed in Fig. 2 by overlapping XRD patterns corresponding to homogenized specimens and to homogenized and tempered specimens, respectively. Fig.2 shows that after homogenization (1073 K/ 18 ksec/ water) the typical structure of Cu-21.6 Zn-7 Al (mass. %) SMA contains four β'_2 martensite plate variants as well as a small amount of β_2 retained austenite
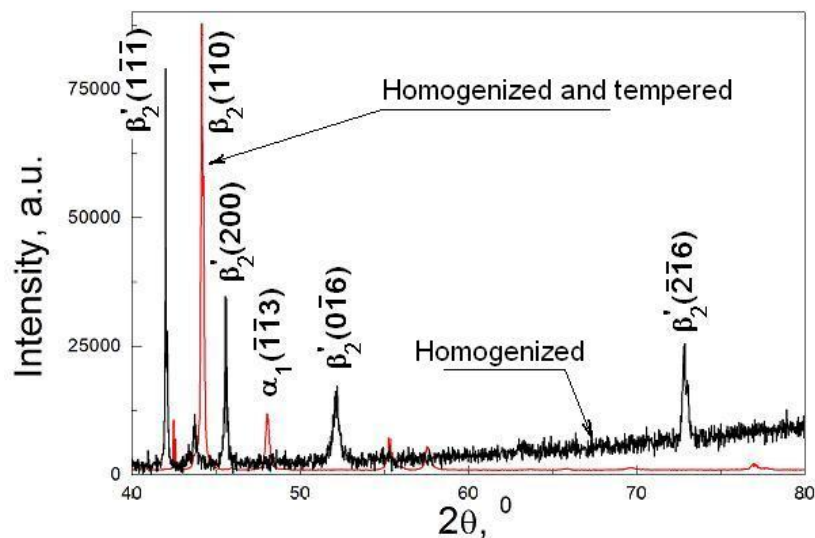

Fig. 2 XRD patterns revealing α_1 bainite formation as an effect of tempering the homogenized specimens

Therefore post-homogenization water quenching enables the formation of an almost fully martensitic structure. After tempering (573K/ 300 sec/ water), it is assumed that most of the martensite transformed to austenite, the amount of which markedly increased, a small part of martensite turned to α_1 bainite, which was identified by means of ($\bar{1}\bar{1}3$) peak, while the rest of martensite became stabilized and remained untransformed [13].

In both specimens no equilibrium face centered cubic (fcc) α-phase was detected. According to the time-temperature transformation (TTT) diagrams, the isothermal transformation for 300 sec. at 573 K of a Cu-21.6 Zn-7 Al (wt. %) SMA is too short as to allow α-phase precipitation [7]

3.3 Microscopic metallographic observations

The typical micrographs, of homogenized and tempered specimens, recorded by OM and TEM are illustrated in Fig.3.
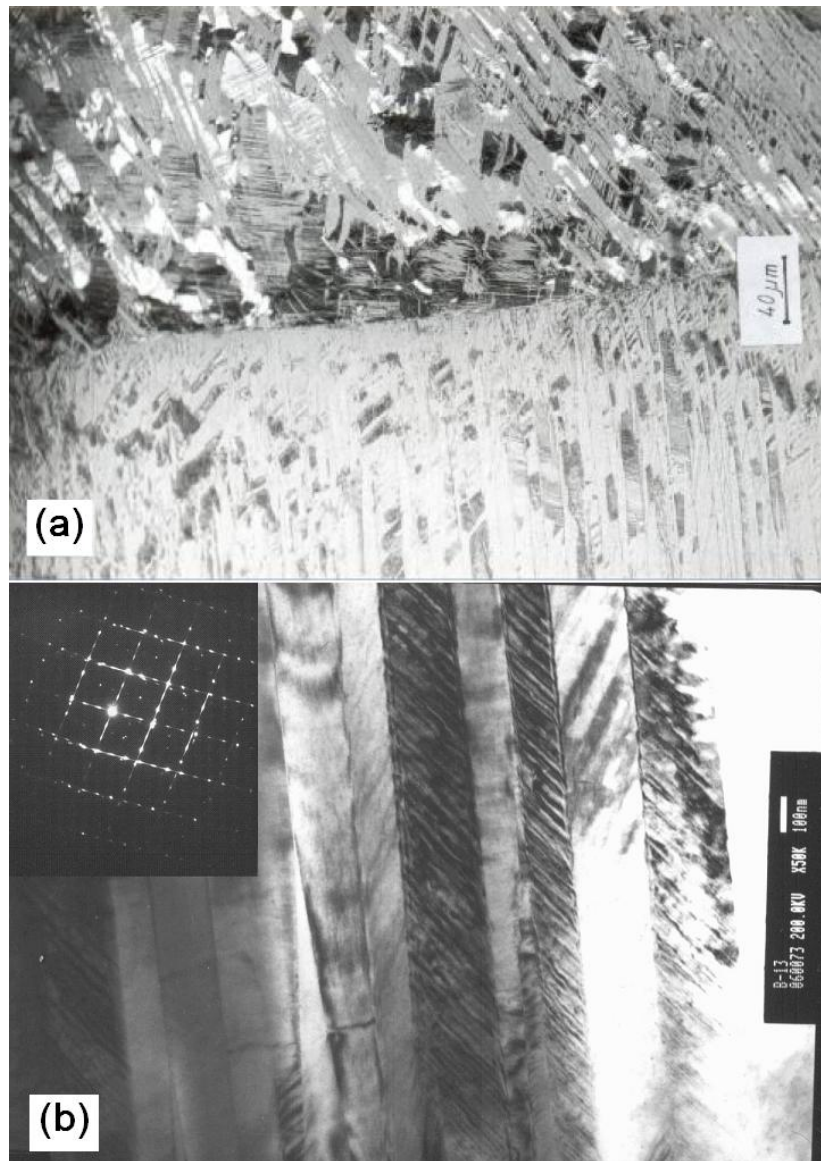

Fig. 3 Typical micrographs illustrating bainite structure and morphology, in a homogenized (1073 K/ 18 ksec/ water) and tempered (573K/ 300 sec/ water) specimen of Cu-21.6 Zn-7 Al (mass. %) SMA, by means of: (a) OM; (b) TEM

The OM micrograph from Fig. 3(a) reveals a plate-like transformation product with internal striations [14] which seem to be irregularly distributed and have the appearance of microtwins [15], which is characteristic to bainite. It is noticeable that not all of the bainite plates, in upper grain, have internal striations yet some of the plates have extremely fine striations under the form of sub-plates, which could be caused by large dislocations densities [16]. The plate-shaped product and specific area diffraction (SAD) pattern recorded by TEM in Fig. 3(b) correspond to α_1 9R-orthorhombic bainite [17]. Both micrographs confirm previous assumption since no equilibrium fcc α-phase was noticeable

4. CONCLUSIONS

By means of DSC and DTA measurements it has been shown that the transitory formation of α_1 bainite occurred between approx. 535 and 651 K, during the heating of a homogenized (1073 K/ 18 ksec/ water) Cu-21.6 Zn-7 Al (mass. %) SMA. Bainite was formed as a precursor of equilibrium α-phase, being characterized by specific enthalpy absorption of approx. 14 kJ/ kg.

The presence of α_1 ($\bar{1}\bar{1}3$) bainite, as an effect of tempering (573K/ 300 sec/ water) the homogenized specimens, was revealed by means of the corresponding XRD patterns. In good agreement with DSC and DTA measurements, is has been assumed that during heating the largest part of β'_2 martensite reverted to β_2 austenite, a small of martensite transformed to transitory α_1 bainite while the rest became hyperstabilized and experienced reversion at much higher temperatures [18]. In accordance with DSC and DTA results, no α-phase precipitation occurred after tempering at 573 K.

On OM micrographs α_1 bainite revealed plate-like morphology with internal striations, while TEM micrographs confirmed the preservation of plate-shaped form and characteristic SAD pattern for 9R orthorhombic α_1 bainite in Cu-Zn-Al SMAs.

ACKNOWLEDGMENTS

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