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IN-SITU EBSD OBSERVATIONS OF MARTENSITIC PHASE TRANSFORMATION AND RE-CRYSTALLISATION PROCESS

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Robert Chulist's main research area is focussed on smart metallic materials exhibiting a martensitic transformation and related effects such as shape memory effect, magneto-caloric effect and super- and pseudoelasticity. This activity has been manifested in various research projects and publications in the field of martensitic transformation. Concurrent with the main topic related to Ni-Mn-Ga he is investigating high entropy and Fe-based shape memory alloys. Furthermore, the experience gained doing research with synchrotron radiation and EBSD was used for the investigations dealing with explosively joint clads such as AlTi, AlMg, CuTi, stainless steel with Ta and Zr and multi-layer systems. His research activities was recognised by the Foundation for Polish Science with a "Homing Plus" scholarship for young outstanding researchers coming back from abroad. A similar scholarship was obtained for outstanding young scientists granted by Ministry of Science and Higher Education in Poland. In terms of academic papers, the research and findings have been manifested in various publications including 151 articles published in SCI journals (82 articles were published in the last five years).

1. ABSTRACT

The paper presents a series of *in-situ* SEM-EBSD experiments mainly devoted to Ni-Mn-Ga shape memory alloys and pure Al. Firstly, orientation relationship between austenite and martensite during phase transformation of Ni-Mn-Ga alloys has been investigated by *in-situ* EBSD measurements. In the next step, the interface between the austenite and twinned martensite was directly visualised and mapped using a temperature gradient. Depending on the distance from the interface, three distinct types of martensite crystal lattices and their transformation path were revealed. As a result, a new concept for adaptive structures is proposed having regard to a sequential form of martensitic transformation. Then employing the heating stage and EBSD, a precise method for the orientation process of Ni-Mn-Ga-based single crystals was demonstrated. In a further step, *in-situ* experiments dealing with the so-called twin boundary engineering are shown. Depending on the twin configuration (parallel, perpendicular or mixed), different effects can be observed, e.g., magneto-elasticity, magneto-plasticity, and magnetically induced pseudoelasticity. Finally, the re-crystallisation process in pure Al has been studied.

2. INTRODUCTION

So far, the Heusler alloy, Ni_2MnGa close to stoichiometric composition, yields the largest magnetic field-induced strain (MFIS). This alloy shows length changes on the order of 12 % for moderate magnetic fields of about 0.4 at frequencies on the order of 1 kHz [1-8]. The change in length is produced by the movement of twin boundaries in the martensite state. The martensitic phase originates from the transformation of the high-temperature cubic phase (austenite) to the low-temperature, low-symmetry structures [9-11]. However, what distinguishes this system from other shape memory alloys is the extremely low twinning stress on the order of 0.01 - 0.5 MPa [12-14]. In fact, the extremely low twinning stress and MFIS observed in NiMnGa-based single crystals make them a unique system and have raised great research interest both in terms of the crystallographic nature of modulation, martensitic transformation and twinning mechanisms. Therefore, in this paper, the attention is drawn to *in-situ* experiments that unveil the austenite / twinned martensite interface in terms of microstructure and phase crystallography. This particular group of alloys is chosen due to the thermos-elastic nature of the martensitic transformation having its origin in crystallographic reversibility.

The reported in the literature models dealing with the orientation relationship (OR) are mostly based on experimental results such as Bain [15], Nishiyama-Wassermann [16, 17], and Kurdjumov-Sachs [18], or on the phenomenological theory of martensite crystallography proposed by Wechsler, Lieberman and Read [19] and by Bowles and Mackenzie [20]. All of them describe this transformation just as a rigid rotation of the lattice by some angle about a specific axis, or by an invariant plane strain accompanied by a small dilatation.

The common feature for all of them is an invariant plane, referred as to habit plane, which is undistorted and non-rotated with respect to both phases. The Bain description is the simplest one explaining the fcc to bct transformation as a 45° rotation about the main cubic axes of the austenite. As a matter of fact, it describes only the Bain distortion involving a uniform compression along the a-axes and expansion along the c-axis as it is in the case of non-modulated (NM) Ni-Mn-Ga-phase. Since this model disregards the rigid body rotation upon martensitic transformation, it results in only three martensitic variants with the tetragonal c-axis parallel to the main cubic axes of austenite.

Two other models frequently used in literature, assume a constant rigid body rotation involving rotation of 90° about the direction and 95.27° about a common $\langle 1+2+3, -1+2+3, 2\rangle$ for Kurdjumov-Sachs and Nishiyama–Wassermann giving twenty four and twelve possible orientations of martensite variants, respectively. A characteristic feature, common to all, is a symmetrical distribution of martensite variants around the main cubic axes of austenite. As the martensitic transformation involves both the lattice distortion (Bain distortion) and one achieved by a lattice invariant deformation (by slip or twinning), both types of deformation affect the final microstructure and variant orientation. The Bain strain is commonly accepted in literature and it can be easily proven by comparing the crystal structure of austenite and martensite phases. The situation is completely different when it comes to OR between the parent and product phases. Depending on the model used, the type of alloy, the crystal structure, the complex microstructure or the level of twinning stress, smaller or larger deviations from these models are observed. In fact none of the given models describe this relation in a satisfactory way. Therefore, the generally accepted practice is to compare the obtained results with existing models. As a result, the model that has the smallest possible standard deviation is assumed.

The same holds for another method frequently used to calculate and reconstruct the austenitic phase from experimentally measured martensitic orientations [21-23]. This method allows predicting the austenitic orientation based on the measured orientations of martensitic variants. However, as was shown in [24], such an approach often gives a strong deviation from the experimentally measured orientations since it strongly depends on the model used.

On the other hand, modern research techniques such as *in-situ* electron backscatter diffraction (EBSD) or synchrotron radiation combined with a heating stage, and a specific software offer a very high angular resolution on the order of 0.1º. This method seems to be most suitable to verify and complete the existing models describing this relation. Therefore, in this paper the attention is focussed on the detailed OR determination between the austenite and martensite in Ni-Mn-Ga single crystals. For comparison, OR is measured for two different martensite crystal structures, i.e., non-modulated tetragonal and 10M modulated monoclinic phases. Since the obtained results on single crystals are quite controversial, the same relation is determined in a polycrystalline material. In this context, parameters such as different transformation modes, lattice parameters, microstructures, magnetic properties and twinning stress are taken into account. The other issue is the transformation sequence and transformation path during the formation of martensite. Using temperature gradient an austenite / twinned martensite interface is stabilised revealing the crystal structure and microstructure of both phases as well as the transformation sequence across the interface. *In-situ* EBSD measurements combined with the so-called pattern matching show that the lattice mismatch formed at a habit plane is compensated by the formation of micro-twinned and branched martensite along with an elastic change of lattice parameters. EBSD experiments clearly indicate that the crystal structure detected at the interface is very different from the fully transformed martensite and cannot be defined by the so-called adaptive concept [25].

The very low twinning stress and the magneto-crystalline anisotropy in Ni-Mn-Ga system give also rise to many other effects such as magneto-elasticity, magneto-plasticity, and magnetically induced pseudoelasticity. These effects are based on the design and creation of various twin configurations for particular applications. Depending on the twin configuration (parallel, perpendicular or mixed) different effects can be observed. For this reason, in-situ deformation experiments combined with a high-resolution scanning electron microscope allow observing twin boundary motion and, in particular, directly seeing twin – twin interactions including different kinds of twin boundaries.

In the last part, the re-crystallisation process in Al single crystalline material is shown. In order to reveal the formation of new grains separated by high-angle grain boundaries a stable goss orientation is used.

Overall the paper presents some examples of the use of EBSD technique in shape memory alloys and re-crystallisation process using mainly heating and tension/compression stages. The presented results show how to enhance our knowledge in the field of martensitic transformation, mechanical twinning concerning especially functional smart materials, and effects such as MFIS, superelastic strain and magneto-elasticity, magneto-plasticity, and magnetically induced pseudoelasticity. In particular, they aim to answer the question of what is the nature of small periodic atomic displacement in modulated phases, what is the mechanism for extremely low twinning stress in this system, and what is the mechanism responsible for stress-induced martensitic and inter-martensitic transformation. Additionally, heating experiments will show the re-crystallisation process in pure Al and the formation of high-angle grain boundaries (HAGB) in single crystalline deformed material. To confirm the local EBSD measurements the obtained results are compared with synchrotron diffraction experiments.

3. *EXPERIMENTAL PROCEDURE*

Ni-Mn-Ga single crystalline and polycrystalline alloys were obtained by induction melting in an argon atmosphere of elements with purity > 99.99 %. The obtained ingot was re-melted three times due to homogenisation. Then the modified Bridgeman method was used for growing a single crystal material with an induction furnace under vacuum conditions in order to avoid any reaction during melting. For the sample orientation process, EBSD measurements were performed using a high-resolution field emission FEI FEGSEM Quanta 3D equipped with an EBSD detector and then samples were cut along the {100} planes of the parent $L2_1$ cubic phase. Additionally, to induce the austenitic phase and conduct in-situ analysis a Murano 525 heating stage manufactured by Gatan was used. Samples for EBSD measurements were initially prepared roughly on abrasive papers, then they were polished on a canvas with slurries, and finally, they were electropolished using a mixture of perchloric acid and ethanol. In addition, the training process was carried out on an endurance machine. The *in-situ* X-ray experiments were conducted by diffraction of high-energy synchrotron radiation (87.1 keV) in transmission geometry using the HZG materials science beamline P07B at DESY in Hamburg, Germany [26, 27].

4. *RESULTS AND DISCUSSION*

There are several models in the literature detailing OR between the austenitic and martensitic phases. The two most famous relations are the KS and NW and are presented along with the simple Bain model in Fig. 1 for a cube-oriented single crystalline sample (in austenite).

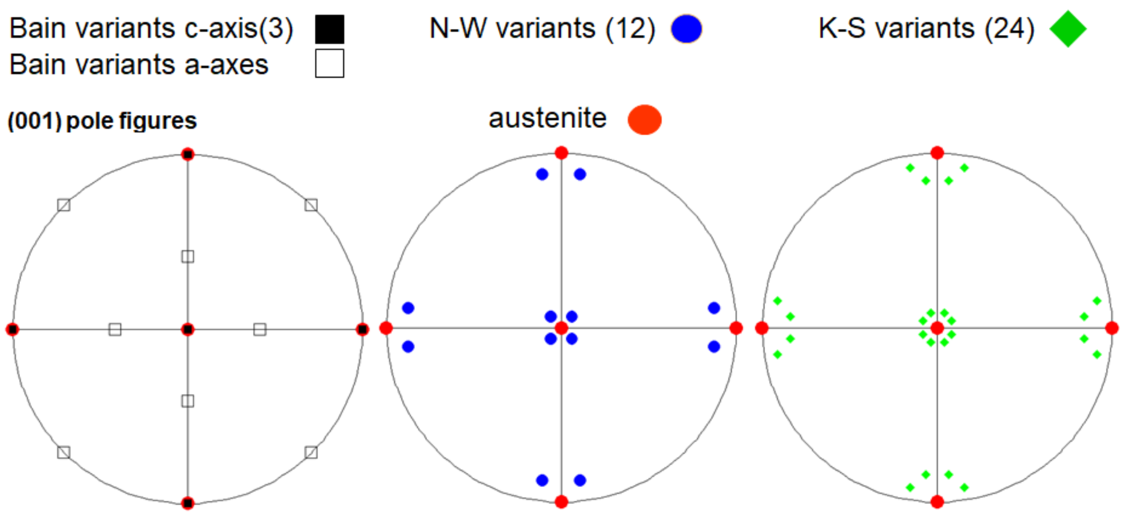

Figure 1. Schematic illustration of three different models defining OR between austenite and martensite.

As was already mentioned, all of them present symmetric distribution of martensitic variants around the austenite orientation. However, when studying the OR between austenite and martensite in non-modulated Ni-Mn-Ga single crystals, a strong asymmetric in terms of the orientation of martensitic variants in the self-accommodate state was revealed [24]. Based on *in-situ* EBSD measurements, it is shown that a single austenitic grain may transform into

24 different tetragonal variants. Combining the microstructural and crystallographic orientation information a hierarchy of twin boundaries was found. This specific sequence results in a hierarchy in the martensite variant formation itself affecting the final orientation of particular martensitic variants.

Further investigations on OR between austenite and martensite have shown two characteristic arrangements of martensitic variants. The so-called macro- and nano-twins represent two groups of variants differently misoriented with respect to each other [28]. The first group was composed of macro-variants that do not follow twin relations due to nano-twinning and are associated with that rigid body rotation, while the latter one consists of minor variants that satisfied the twin relations perfectly. In order to clarify this issue experiments on polycrystalline material were performed.

Figure 2 shows two orientation maps taken at room temperature and 100 °C, respectively. On the left side (Fig. 2a), a typical self-accommodated microstructure with a large number of martensitic variants can be observed. Different regions of the sample transform to various martensitic variants in such a manner that there is no macroscopic shape change. On the other hand, Fig. 2b shows three austenitic grains with different orientations that can be easily recognised by different colours. Interestingly, the OR between austenite and martensite in polycrystalline samples is symmetrical. It seems that this symmetrisation occurs due to grain constraints that did not permit a free rotation and it “tied up” the orientations of martensitic variants in the close vicinity of austenite. Thus, the OR between austenite and martensite for single crystalline and polycrystalline samples is different for the same compositions. It should be mentioned that the misorientation between austenite and martensite for single and polycrystalline material is fully reproducible being measured many times using also a large number of samples. Additionally, the samples were stuck with highly elastic glue to avoid any additional constraints coming from the heating plate.

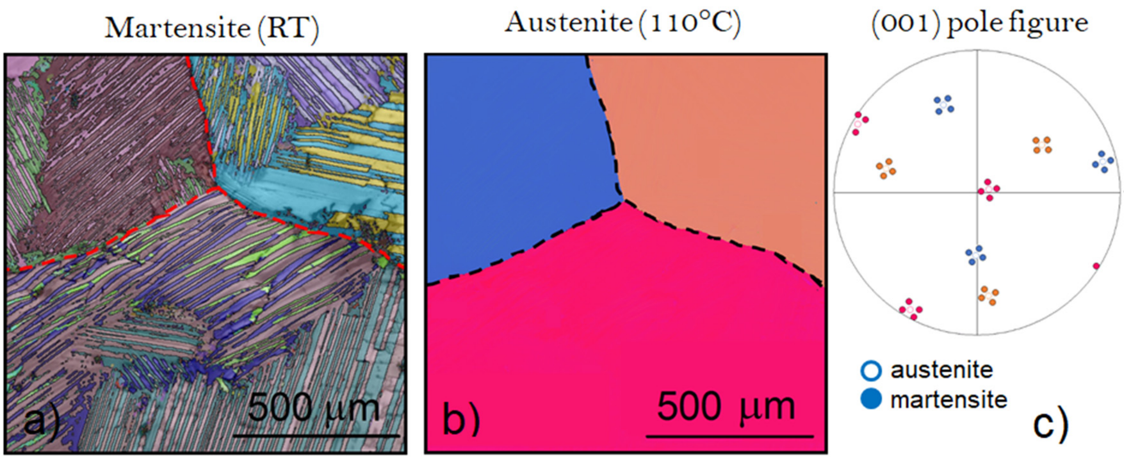

Figure 2. EBSD maps taken at a) room temperature, and b) 100 °C of Ni50Mn31Ga non-modulated sample along with c) a superposition of the (001) pole figure for austenite (open circles) and martensite.

Next, the crystal structure and transformation sequence in 10M Ni-Mn-Ga martensite was studied. This experiment was conducted using a temperature gradient to stabilise the austenite / twinned martensite interface. In order to validate the so-called adaptive concept for 10M Ni-Mn-Ga alloys, bulk single crystalline samples were subjected to *in-situ* measurements using EBSD. The concept of adaptive martensite proposed more generally by Khachaturyan *et al.* [25] and particularly to 14M Ni-Mn-Ga alloys by Kaufman *et al.* [29] assumes that the lattice mismatch formed at a habit plane can be compensated by nano-twinned martensite formation. The *in-situ* experiments revealed that depending on the distance from the interface three distinct types of martensite crystal lattice were observed: simple tetragonal, and two monoclinic modulated, i.e., 10M' and 10M were shown. It is demonstrated that the lattice mismatch formed at a habit plan is to a larger extent compensated by the formation of micro-twinned and branched martensite along with an elastic change of lattice parameters. Figure 3 demonstrates a Kikuchi pattern taken in the austenite and martensite regions including the interface and shows the evolution of crystal structure and lattice parameters across the interface. It is clearly visible that the crystal structure differs significantly from that registered about 1 mm from the interface (classic 10M martensite). Overall the experimental results show the crystal lattice does not adapt a modulated phase at the habit plane and cannot be built from simple non-modulated tetragonal blocks but rather an independent modulated crystal phase in which a specific sequence of phase transformations takes place employing a shear/shuffling concept.

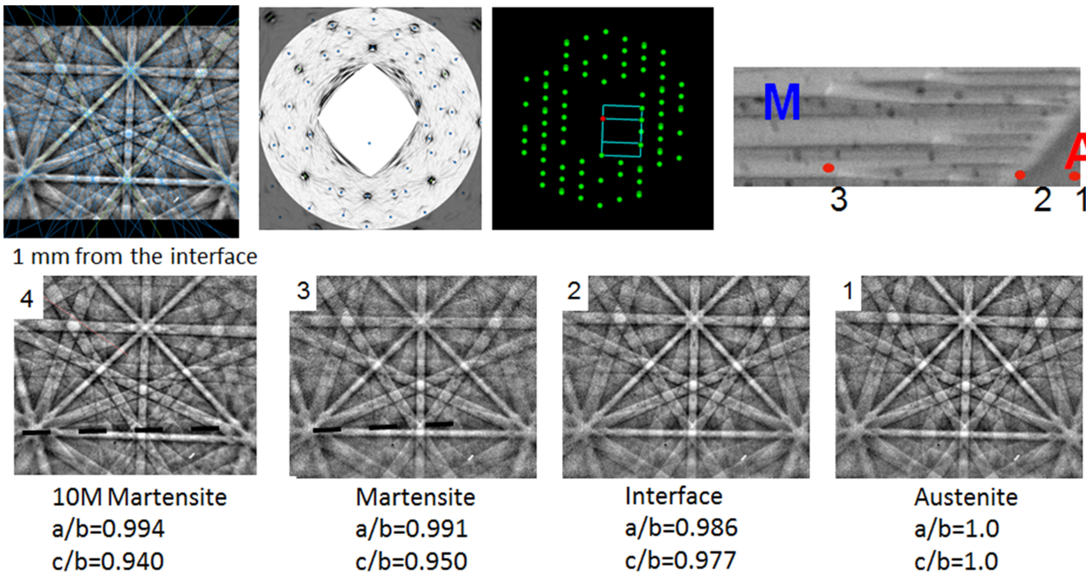

Figure 3. Austenite-martensite interface measured with high-resolution EBSD system along with the so-called pattern matching which allowed following very precisely the crystal changes.

In the next part, the determination of orientation of single crystalline material was performed. These *in-situ* heating experiments aimed to provide much more precise control for cutting single crystals as compared to measurements based on the multivariant state at room temperature. It is shown that the measuring orientation in the high-temperature phase (austenite) leads to a much more precise final orientation. This, in turn, maximizes Schmid factor, increases the given strain, and decreases the twinning stress having a great impact on the functional properties of these alloys. For these reasons, the orientation process in the austenite phase is more effective independently of the orientation relationship or the transformation mode.

The next part of the in-situ experiment is dealing with the so-called twin boundary engineering. The main idea is presented in Fig. 4 where according to the twin configuration (parallel, perpendicular or mixed) different effects can be obtained, e.g., magneto-elasticity, magneto-plasticity, and magnetically induced pseudoelasticity.

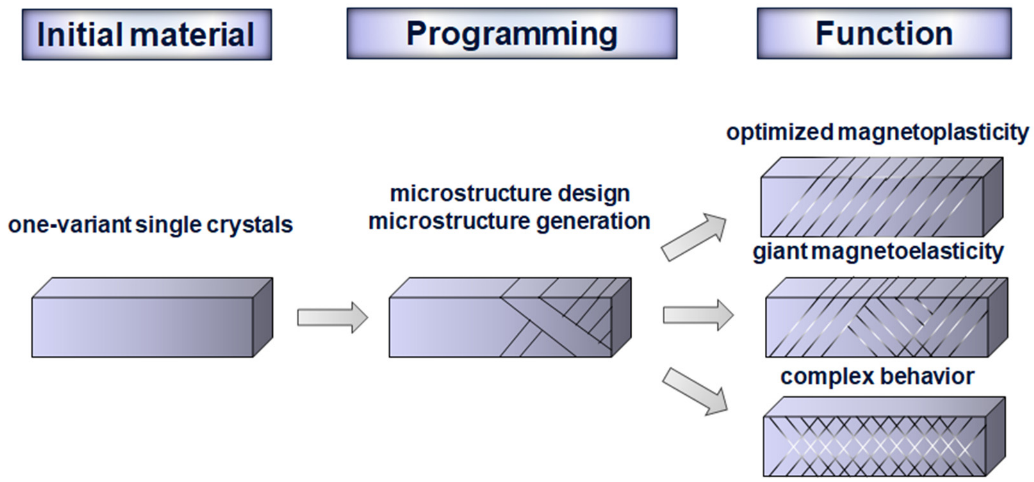

Figure 4. Schematic diagram of programming functions obtained using the so-called twin boundary engineering.

For instance, densely twinned microstructures are beneficial for actuator applications due to repeatability, stability and long fatigue life. The so-called polysynthetic twins were created by a bending method. As a result, a fine-twinned laminated microstructure was formed consisting of pure type I twin boundaries. These results were confirmed not only by EBSD measurements but also by X-ray conventional and synchrotron diffraction. Due to its single type of twin boundary and a relatively small distance to cover by a single twin boundary, this microstructure is characterised by fast MFIS and better repeatability and stability. Our other study on perpendicular twin boundaries has explained the mechanism of a pseudoelasticity of about 3 % in a triple twin configuration [30]. Extremely low twinning stress also promotes the tapering of twin planes. This in turn enables a whole spectrum of super- and pseudoelastic effects that will be presented too.

In the last part of the presentation experiments with Al and the re-crystallisation process will be shown. For this reason, a stable Goss orientation (110)[001] is used. Single-oriented samples were subjected to plane-strain compression up to 60 % in channel-die.

A stable orientation was chosen since these orientations exhibit a very small misorientation spread even if subjected to large deformation. Thus, they do not decompose and do not create new orientations that can affect the re-crystallisation process. This study was designed to show that also orientations different than the existing in the deformed state may grow during the re-crystallisation process. Such an approach would have permitted to complete the theory of re-crystallisation that assumes that only orientations that exist in the non-recrystallised sample may grow during the re-crystallisation process. Therefore, in this experiment, a highly deformed microstructure with a large number of low-angle grain boundaries (LAGB) was used (Fig. 5). Subsequently, this material was heated up to 223 °C with a 5° step starting at 193 °C. At this temperature, new grains with completely new orientations start to appear. This experiment confirms that new orientations, which are not present in the deformed matrix, may nucleate. As a result, an additional approach for the creation of new grains is proposed.

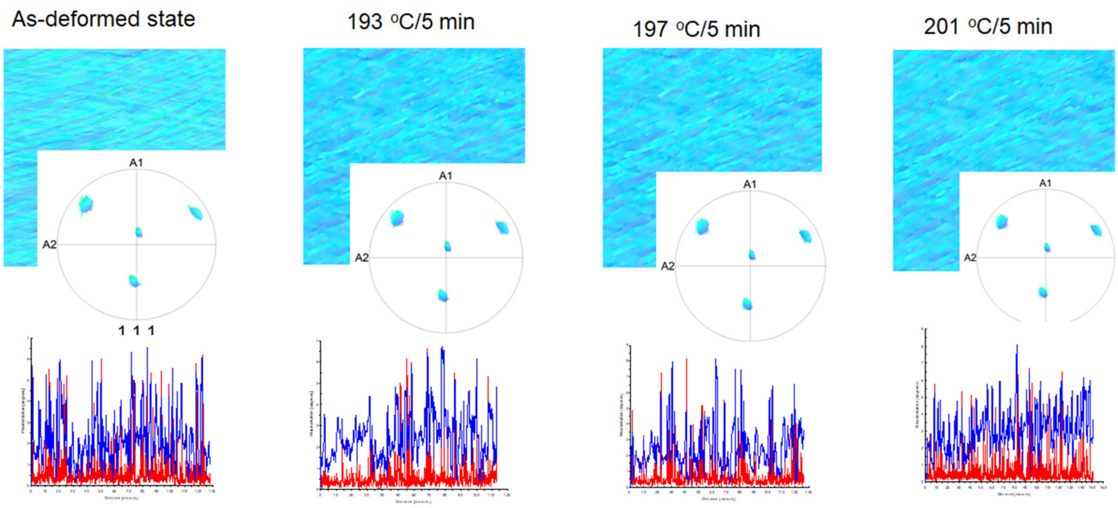

Figure 5. *In-situ* SEM-EBSD heating experiment performed at different temperatures for Al of (110)[001] initial orientation, deformed up to 60 % in channel-die.

5. *CONCLUSIONS*

The paper presents a series of *in-situ* SEM-EBSD experiments devoted to Ni-Mn-Ga shape memory alloys and pure Al. It is shown that orientation relationships between austenite and martensite in the Ni-Mn-Ga system is different for single crystalline and polycrystalline samples. Single crystals exhibit a strong asymmetry in variant distribution, while due to grain constraints, a symmetric distribution of martensitic variants in polycrystalline Ni-Mn-Ga is demonstrated.

The experimental results show the crystal lattice does not adapt a modulated phase at the habit plane and cannot be built from simple non-modulated tetragonal blocks but rather an independent modulated crystal phase in which a specific sequence of phase transformations takes place employing a shear/shuffling concept. Employing EBSD at a higher temperature (in austenite state) provides much more precise orientation control for cutting single crystals as compared to measurements based on the multivariant state in martensite. Depending on the twin configuration (parallel, perpendicular or mixed), different effects can be observed, e.g., magneto-elasticity, magneto-plasticity, and magnetically induced pseudoelasticity. Finally, re-crystallisation process in pure Al has been analysed showing the formation of new orientations in the homogenously deformed matrix. Overall, the in-situ experiments show a huge potential of EBSD technique in studying shape memory effect and related phenomena. This method also provides a very powerful analytical tool for analysing the re-crystallisation process and grain growth kinetics of metallic materials.

6. *ACKNOWLEDGEMENTS*

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