Adolf Martens and the Research on Martensite

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1. Introduction and overview

Adolf Martens is considered together with personalities like Le Chatelier, Howe, Osmond, Roberts-Austen, Sorby, Stead and Tschernoff as one of the founders of metallography in the 19th century (1). On occasion of the 75th anniversary of his death, a short portrayal of his life and work is presented. In addition to the retrospect, the present state of research on martensite with respect to the basic classes of materials - metals, ceramics and polymers - as well as the study on biological martensitic transformations is illustrated in brief by some examples.

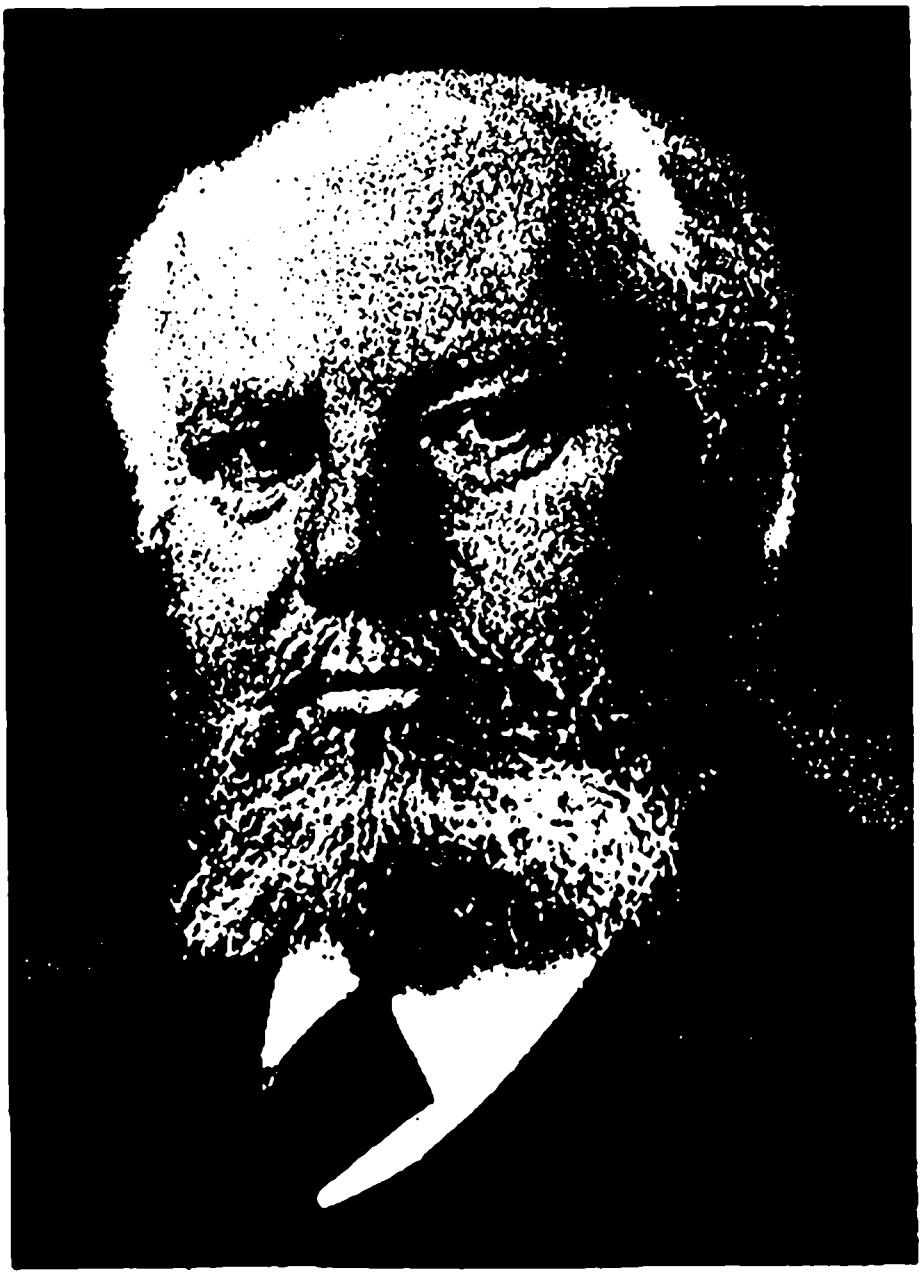

Fig. 1:
Adolf Martens
(1850-1914)

Article available at http://www.esomat.org or http://dx.doi.org/10.1051/esomat/198901001

2. The life of Adolf Martens

Adolf Martens, born March 6, 1850 in the district of Mecklenburg, received an engineering education at the Royal "Gewerbeakademie" Berlin after a practical training at a machine factory, and joined in 1871 the engineering staff of the Royal Prussian Railways. There he worked in the fields of iron and steel structures and quality control of railway components. In 1880 he became an assistant to Professor Consentius at the Technische Hochschule (TH) Berlin-Charlottenburg and was appointed in 1884 Head of a small Mechanical-Technical Testing Institute at the TH. This institute merged with a Chemical-Technical Testing Institute and a Test Office for Civil Engineering Materials to form in 1904 under the directorship of Adolf Martens the Royal Material Testing Office - a predecessor institute of the present Federal Institute for Materials Research and Testing (BAM). Adolf Martens was appointed Professor in 1889, Member of the Royal Academy of Sciences Berlin in 1904 and received a honorary doctor's degree from the Technische Hochschule Dresden in 1905. After a life full of scientific-technological work and the successful establishment of the Royal Materials Testing Office as one of the leading institutions of its kind worldwide, he died on July, 24, 1914 (2, 3).

3. The work of Adolf Martens

Adolf Martens was a strong personality with immense working and management capabilities, extreme broad technological interest, profound engineering skills and scientific creativity. Figure 1 shows a photograph of him. In his early years, when he worked for the Royal Prussian Railways, he could perform his metallographic work only in his spare time at his own expense. For his studies, he developed by himself the experimental tools he needed, including an optical microscope with a new illumination technique, see Figure 2 (4).

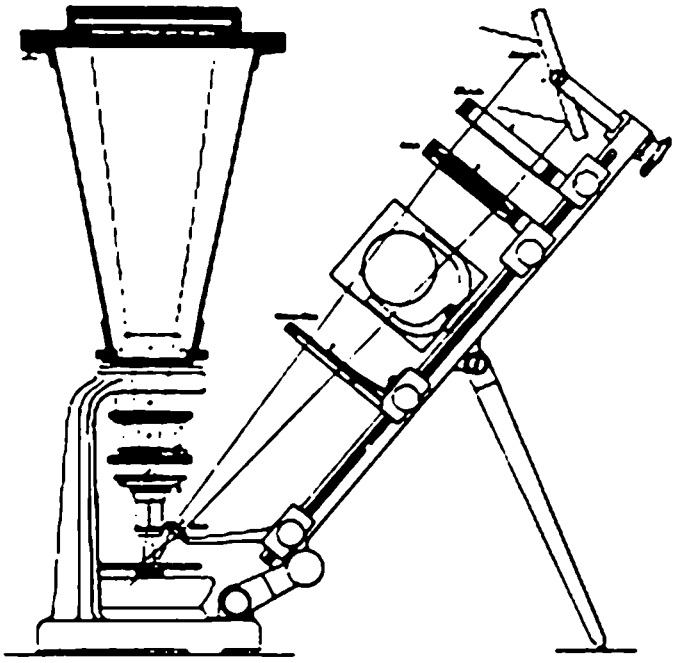

Fig. 2: Optical microscope, designed by Adolf Martens (1880)

Krystalldruse.

Tannenbaumförmiges Eisenkrystall

Spiegeleisen II. Rolandshütte
Schliff mit schwefelsaurer Magnesia angeätzt

Kennell
Schliff mit schwefelsaurem Kupferoxyd angeätzt

Tannenbaumförmiges Eisenkrystall

A. Martens:

Ueber die mikroskopische Untersuchung des Eisens.

Fig.3 Microstructural investigation of iron

Because at this time it was very difficult to obtain microphotographs of good quality, Martens made very accurate drawings of the microstructures with the help of a special optical prism attached to the microscope. Later, in collaboration with the Carl Zeiss establishment he designed "what was to be the best equipment for metallographic photomicrography for several decades" (1).

He studied fractured as well as polished surfaces and developed special etching techniques to visualize specific microstructural features, see Figure 3. He compiled the results of his studies meticulously in his technical note books. Figure 4 shows a page of his note books.

In addition to his metallographic studies and the development of the connected apparatus and techniques, he designed instruments and techniques for other areas of materials research and testing, for example the Martens tensile tester (50.000 kg_f), the Martens scratch hardness tester and the Martens lubricant oil test rig, just to mention a few.

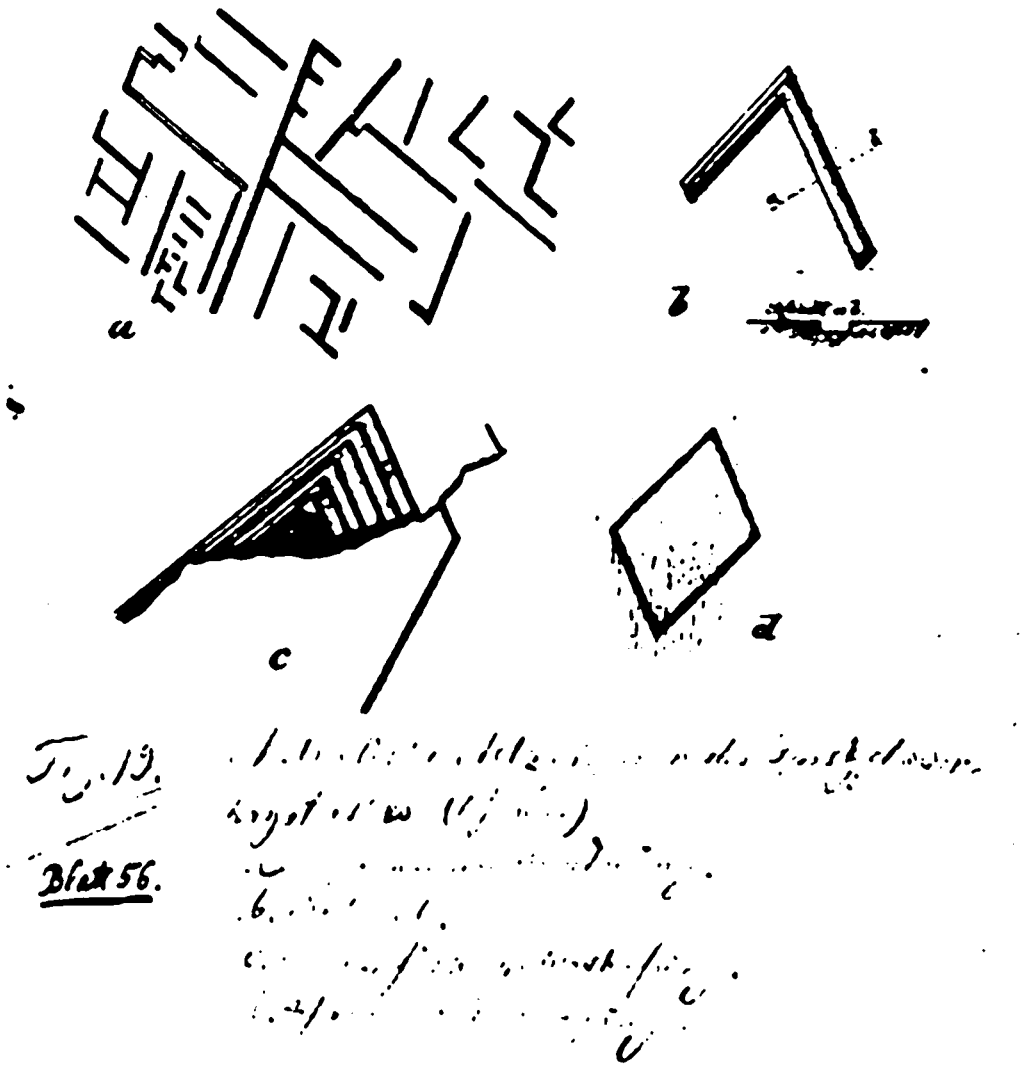

Fig. 4: Microstructure of Spiegeleisen (etched details)

The accuracy of Martens' metallographic studies can be illustrated in comparing his drawings (left) with contemporary micrographs (right) of materials, similar to those he studied. This is shown for the examples of a dendritic structure, Fig. 5, a fracture surface, Fig. 6, and an etched microstructure, Fig. 7, (5, 6, 7).

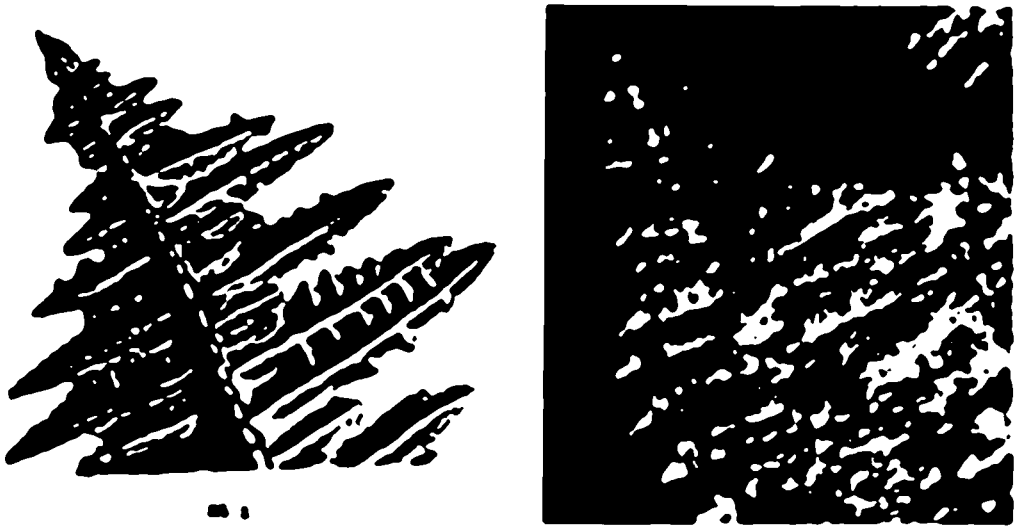

Fig. 5

Fig. 6

Fig. 7

The research results and publications of Martens - which cannot be reviewed within the scope of this paper - received considerable interest by his colleagues, so that Osmond termed the "martensitic" structure of steel after him (8). Although Adolf Martens published no own studies connected directly with the microstructural constituent of steel which bears his name, attention should be drawn to the microstructural drawing by Martens, shown in Figure 8. This drawing, which can be found in one of his publications (5), shows an impressive similarity to an essential feature of "martensite", namely the inhomogeneous shear pattern of internally slipped martensite plates, see Figure 11.

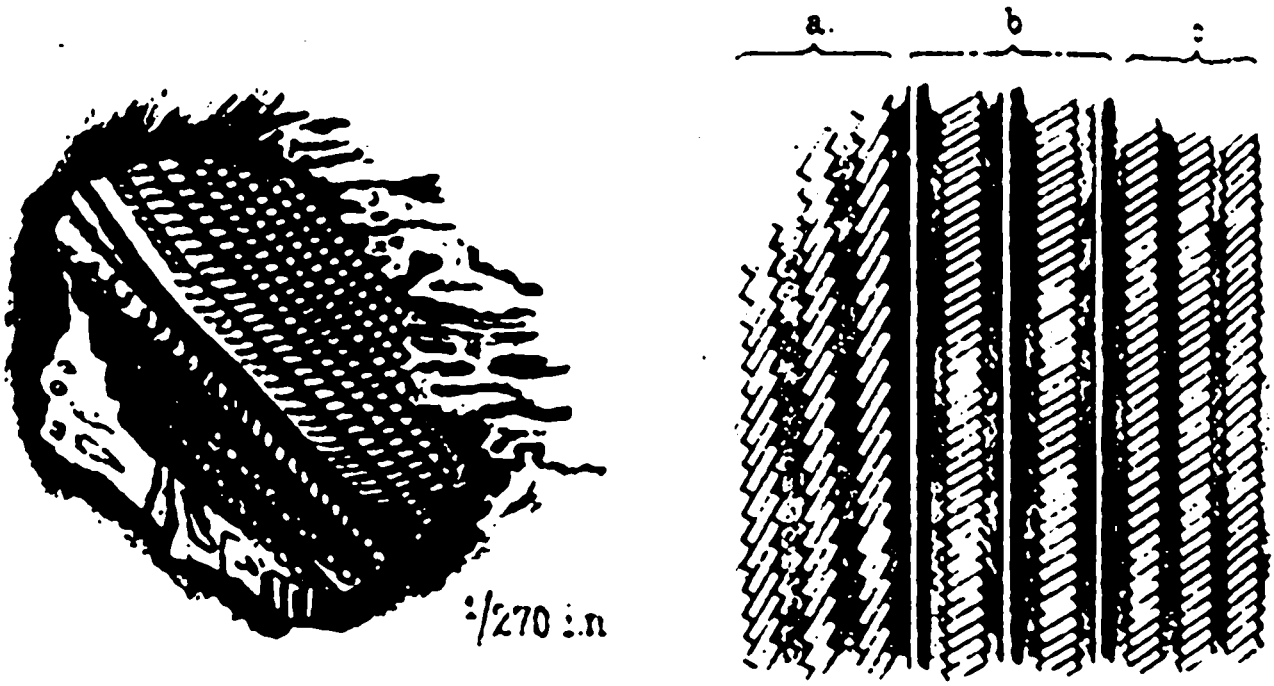

Fig. 8: Microstructural drawings by Adolf Martens

4. Research on martensite today

Nowadays the term "martensite" is used in a wide context to apply to the products of transformations taking place in crystalline solids by coordinated displacements of atoms or molecules over distances smaller than interatomic distances in the parent phase. Martensitic transformations have been observed in all classes of materials - metals, ceramics, polymers - as well as in biological structures, as illustrated briefly in the following.

4.1 Metals

Historically, research on metals, mainly on steels, has led to the development of the phenomenological crystallography theory of the martensitic transformation. According to this theory there are three phenomenological steps describing the total transformation (9):

(i) The Bain distortion: E.C. Bain suggested in 1924 (10) that the austenite(parent phase)-martensite transformation could be explained by a diffusionless homogeneous upsetting of the parent fcc lattice into the required bcc (or bct) lattice, involving minimal atomic displacements, as shown schematically in Figure 9. It was subsequently justified mathematically that the particular correspondence between lattices envisioned by Bain involves the smallest principal strains.

(ii) Inhomogeneous shear: In conjunction with the Bain distortion, a lattice invariant deformation, such as slip, twinning or faulting occurs. This secondary deformation provides the invariant plane condition at the macroscopic scale and maintains a semicoherent glissile interface between the martensite and parent phase.

(iii) The third step involved in the phenomenological crystallography theory of the martensitic transformation is a rigid body rotation.

The combined effect of the three operations (i), (ii), (iii) is equivalent to the experimentally observed shape deformation. There is no time sequence implied as to which occurs when.

In addition to the geometric models, dislocation theories have been recently developed (11). According to these theories, martensitic transformations are defined as a subject of diffusionless/ displacive solid-state transformations in which the strain energy arising from a shear-dominant lattice distortion controls the kinetics and product morphology during transformation. The dislocation description allows the prediction of numerous interfacial properties, including the interfacial stress field, energy, stability and interfacial mobility. Application of the dislocation-based approach to the mechanism and kinetics of martensitic nucleation and growth has led to a reasonably quantitative explanation of the essential features of martensitic transformations.

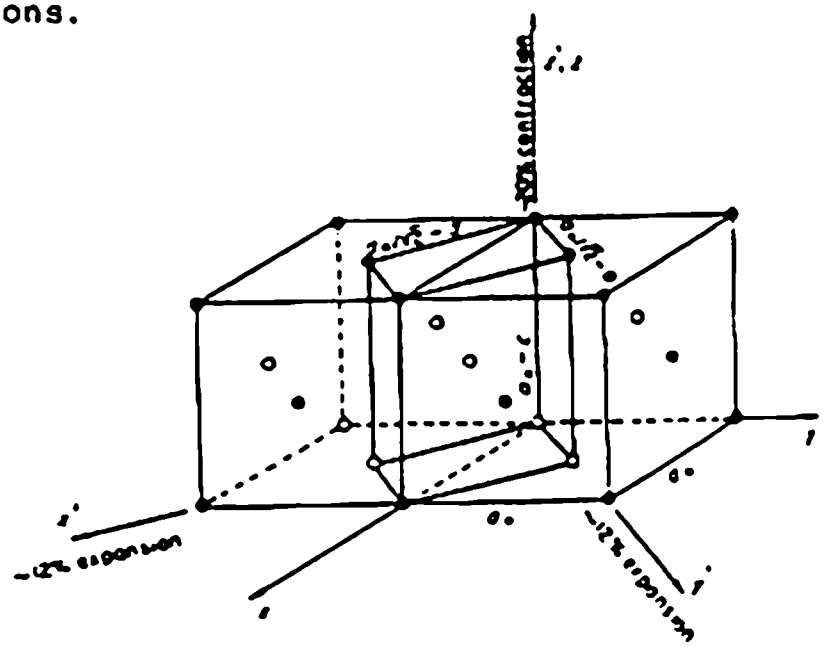

Fig. 9: Bain distortion in iron alloys

4.2 Ceramics

Displacive transformations involving large changes in volume or coordination number occur in ceramics as well as in inorganic compounds and minerals (12), see Table 1.

Ceramics	
Boron nitride: BN	(wurtzite-type ⇌ graphite-type)
Carbon: C	(wurtzite-type ⇌ graphite)
Zirconia: ZrO_2	(tetragonal ⇌ monoclinic)
Inorganic Compounds	
Alkali and ammonium halides:	(NaCl-cubic ⇌ CsCl-cubic)
Nitrates: $RbNO_3$	(NaCl-cubic ⇌ rhombohedral ⇌ CsCl-cubic
KNO_3, $TlNO_3$, $AgNO_3$	(orthorhombic ⇌ rhombohedral)
Sulphides: MnS	(zinc blende-type ⇌ NaCl-cubic)
	(wurtzite-type ⇌ NaCl-cubic)
ZnS	(zinc blende-type ⇌ wurtzite-type)
BaS	(NaCl-type ⇌ CsCl-type)
Minerals	
Pyroxene chain silicates:	
Enstatite ($MgSiO_3$)	(orthorhombic ⇌ monoclinic)
Wollastonite ($CaSiO_3$)	(monoclinic ⇌ triclinic)
Ferrosilite ($FeSiO_3$)	(orthorhombic ⇌ monoclinic)
Silica:	
Quartz	(trigonal ⇌ hexagonal)
Tridymite	(hexagonal, wurtzite-related)
Cristobalite	(cubic ⇌ tetragonal, zinc blende-related)

The typical martensite appearance known from metals is likewise found for certain types of ceramics. For example, a characteristic martensitic microstructure develops by cooling a ZrO_2-Sc_2O_3 alloy from the high-temperature cubic(c) phase region to the β-phase region (13), see Figure 10. The microstructure of the β-phase usually has a "herring-bone" structure, likely to be a favourable one for minimizing the strain energy and interfacial energy associated with the c-β transformation.

In bulk single crystals of zirconia (ZrO_2), the tetragonal to monoclinic transformation was experimentally and theoretically proven to be martensitic.

By exploiting the martensitic phase transformation of discrete zirconia particles dispersed within ceramic matrices, the mechanical properties of brittle ceramics can be improved. The toughening originates from the crack shielding associated with the volume and shape change of the martensitic transformation and reduces the stress intensity at the crack tip. This type of energy dissipation is analogous to that associated with crack tip plasticity in ductile metals. Three basically different classes of ZrO_2-toughened ceramics have been identified (14):

(i) Partially-stabilized ZrO_2 (PSZ), in which tetragonal ZrO_2 particles are coherently precipitated within a cubic stabilized ZrO_2 matrix (precipitation-toughened ceramics)

(ii) Tetragonal ZrO_2 polycrystals (TZP) which consist predominantly of fine tetragonal ZrO_2 matrix grains. These ceramics represent a very strong class of ceramic materials (bend strength > 2000 MPa)

(iii) ZrO_2-toughened ceramics (ZTC), where tetragonal or monoclinic ZrO_2 particles are dispersed in ceramic materials such as Al_2O_3, mullite ($3Al_2O_3 \cdot 2SiO_2$, spinel ($Mg\ Al_2O_4$), etc. (dispersion-toughened ceramics).

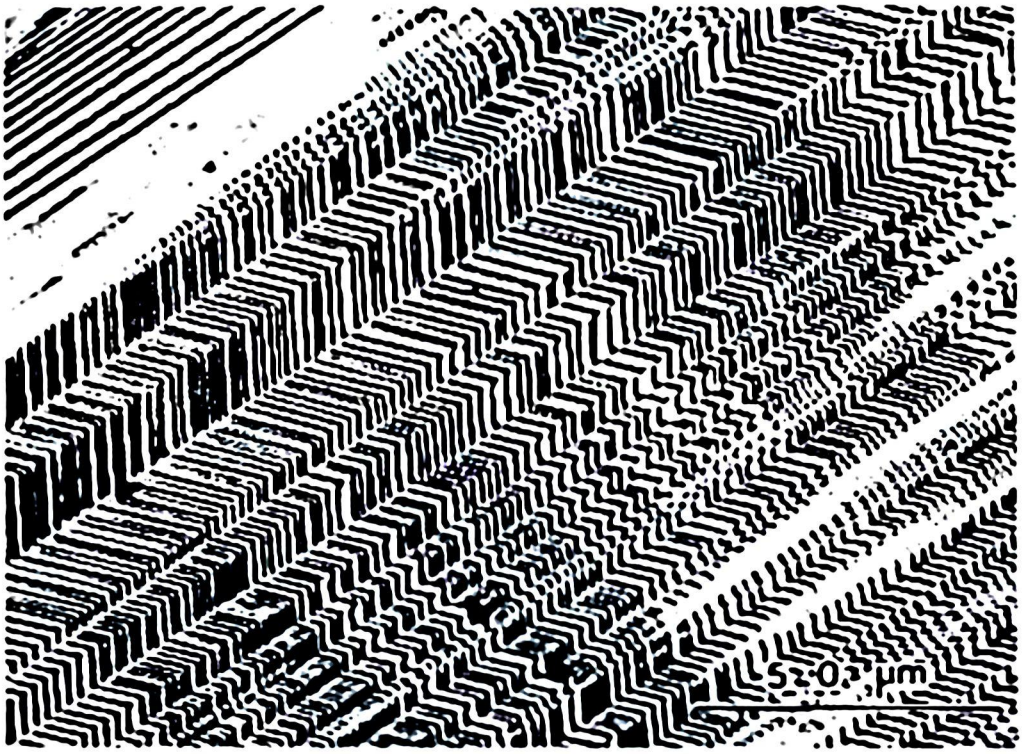

Fig. 10: Herring-bone structure of ZrO_2-Sc_2O_3 (β-phase)

4.3 Polymers

In order to analyze the possibilities of polymorphism in polymers, a survey of the shape changes that can be associated with diffusionless transformations is given in Figure 11 (15).

I. Lattice variant deformation can be composed of
   (i) shear without change in volume
   (ii) volume change without shear.

II. Lattice invariant deformation is always required, if the transformation takes place in the interior of the matrix phase
   (iii) plastic shear by slip or twinning
   (iv) elastic (not shown in Figure 11).

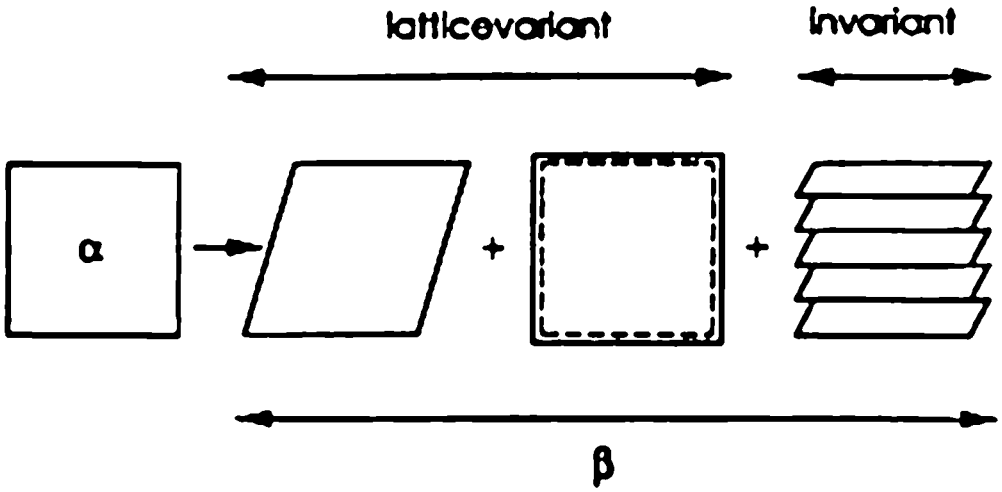

Fig. 11: Shape changes of diffusionless transformations

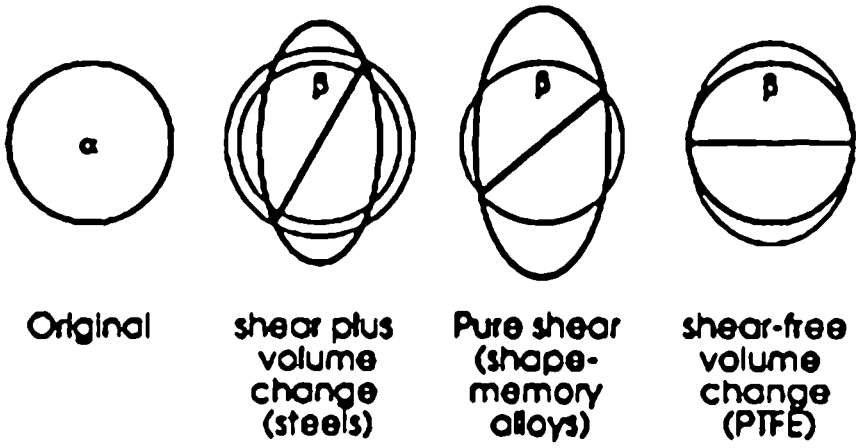

Fig. 12: Possibilities for lattice-variant deformations

The principal cases of lattice variant shear are shown in Figure 12. An example for the general case in which shear and volume change occur simultaneously are iron-base alloys. The shape-memory alloys based on the CsCl-structure (e.g. CuZn, NiTi) come closest to the case of pure shear without volume change. The polymer PTFE is an example for the case in which the volume changes, but no shear can occur. Experiments have shown that the PTFE transforms by a special type of diffusionless transformation that takes place by a shear-free lattice variant volume change and lattice invariant elastic strain (15).

From studies on other organic single crystals it was concluded that a critical resolved shear strain criterion determines which possible deformation or transformation mode occurs on application of unidirectional stress. The magnitude of the shear strain must be small since the configuration of tight fold geometry restricts the operation of large deformation modes. The transformation or deformation mechanism favoured is the one with the simplest shuffles or displacements of molecular chains. For example, in single crystal films of polyethylene under directional tensile stress, the crystallography of the observed deformation modes indicated that twinning, repeated twinning and slip occured in connection with an orthorhombic to monoclinic transformation (12).

4.4 Biological martensitic transformations

Recent research indicates that martensitic transformations are also well represented in biology (11). Figure 13 shows the example of tail-sheath contraction in the T4 bacteriophage, a virus which infects E. Coli bacteria. The virus consists of a DNA-filled icosahedral head or capsid attached to a tail assembly composed of a rigid tail-core, a cylindrical tail-sheath, and a baseplate assembly with six long and short tail fibers. The tail-sheath is a metastable two-dimensional protein crystal closed to form a cylinder. When the tail fibers attach to the appropriate bacterial membrane, they distort the baseplate which, in turn, triggers a strain-induced single-interface martensitic transformation in the crystalline tail-sheath. The transformation shape strain produces a substantial contraction which drives the rigid tail-core through the bacterial membrane, injecting the virus DNA into the bacterium.

Figure 14 depicts a coherency dislocation model of the martensitic interface transforming the protein crystal between the structures corresponding to the extended and contracted states. The helical nature of the cylindrical crystal provides a built-in pole mechanism whereby only a fixed number of dislocations is necessary to spiral up the close-packed rows and completely transform the crystal. The transformation shape strain involves a shear greater than 100%, which not only shortens the sheath but also provides a large twist about the cylinder axis, thus helping the tail-core to "bore" through the bacterial cell wall.

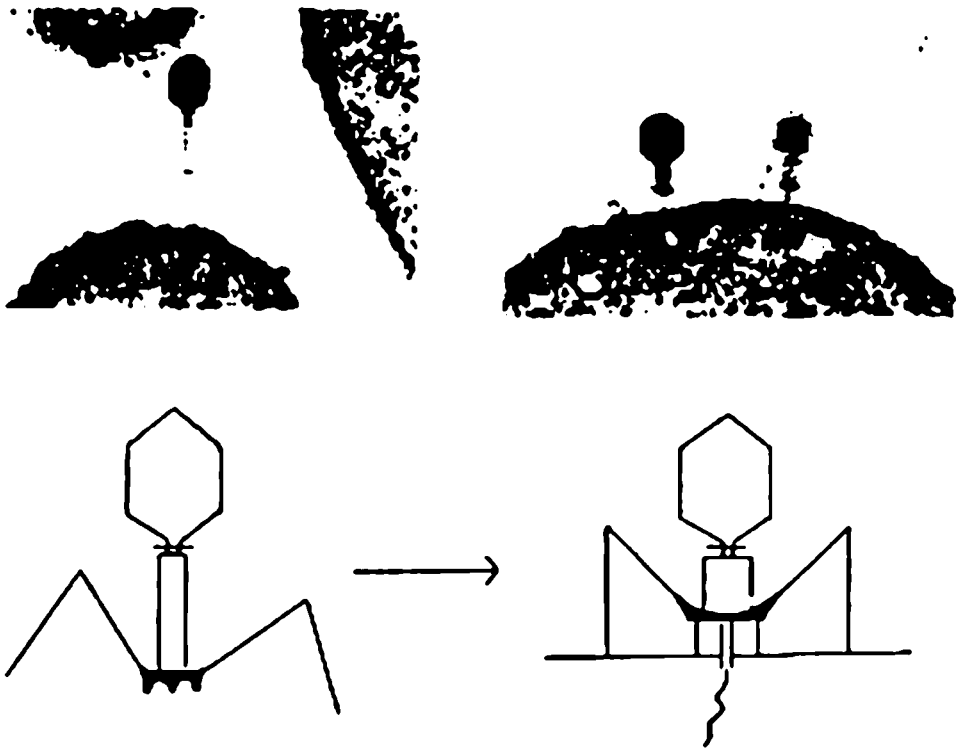

Fig. 13: Bacterial virus tail-sheath contraction

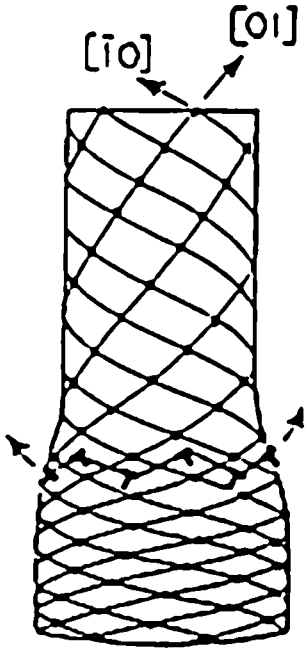

Fig. 14: Virus contraction by martensitic transformation

5. Final remark

The examples from the areas of metals, ceramics, polymers and biology indicate the impact of martensitic transformations not only for materials science and engineering but also for the control of motion and shape in living things. The Federal Institute for Materials Research and Testing (BAM) Berlin is proud that the name of Adolf Martens - one of the fathers of BAM - is connected with this important field of technology and science. This paper is dedicated to his memory.

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