



Editorial

## Microstructures and Properties of Martensitic Materials

## **Cyril Cayron**

Laboratory of Thermomechanical Metallurgy-PX Group Chair, Institute of Materials, Ecole Polytechnique Fédérale de Lausanne, 2000 Neuchâtel, Switzerland; cyril.cayron@epfl.ch

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Martensite, initially named in honor of Adolph Martens and his pioneering work in metallography and microstructures at the end of the 19th century, has now a far broader meaning than previously used. Martensite is the product of a diffusionless shear-like transformation. The papers published in this Special Issue [1–9] confirm that research in martensitic materials is very active. Even the old 'simple' Fe-C alloys keep many secrets that are still beyond the capabilities of modern computers. It is well-known that increasing carbon decreases the martensitic start temperature (Ms), which as for nitrogen, but the effect is not yet fully understood. Beyond the important configurational entropy component brought by this interstitial atom, the contribution of carbon to free energy should be investigated. It is indeed difficult to imagine how the chemical potential is affected, when only 0.5%-at is added to pure iron (i.e., less than one atom of carbon per  $4 \times 4 \times 4$  unit cells of body centered cubic (bcc) iron). Karewar et al. [1] have focused their efforts to simulate, by the use of molecular dynamics, the effect of carbon on the martensitic transformation in the presence of defects. Their study reveals the importance of knowing the mechanism at the atomic scale, and the importance of taking into account the barrier imposed by the resolved shear stress. The effect of carbon is of prime importance in steels; most of their complexity and mechanical properties come from the stable and metastable phases. Zhang et al. [2] have measured the mechanical properties of steels elaborated by quenching–partitioning–tempering in the temperature range 20 °C to 350 °C, and they have systematically investigated the microstructure by X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM). They show that the high strength x elongation product values (that are useful for shock absorption) are the consequences of the complex microstructures made of metastable retained austenite, that transforms into martensite under stress (TRIP effect) and fine dispersion of niobium carbides and iron carbides. The transformation of metastable austenite under stress is a vast subject of research that has not yet reached consensus. Baur et al. [4] have investigated how an austenitic Fe-20Ni-1.2C alloy maintained under four-point flexion transforms when it is placed in fridge at -80 °C (very close to the Ms temperature of the alloy). They observed that martensitic transformation occurs only in the tensile part of the specimen. The authors investigated, by Electron BackScatter Diffraction (EBSD), the martensite variants that were formed, and highlighted that the results could not be explained with the classical Phenomenological Theory of Martensite Crystallography (PTMC). Instead, an empirical variant selection rule, based on plate groups, could be established, but its physical meaning remains to be discovered. The internal microstructure of the lenticular (259) martensite is probably more complex than the simple lattice invariant shear expected from PTMC. Austenite can be transformed into martensite under stress, but the reverse is also true. Aizawa et al. [3] showed by Energy Dispersive Spectrometry (EDS), EBSD, and TEM that, when a martensitic stainless steel is nitrided, the martensite close to the exposed surface is destabilized due to the increase of nitrogen content, and transformed back into austenite, which produces an intriguing nano-laminated austenite/martensite microstructure. Sometimes, the distinction between bcc-martensite and bcc-bainite is difficult to make because the usual C-curve of bainite in the

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Time Temperature Transformation TTT diagram is flat and overlaps with the horizontal plateau of the Ms of martensite. This is the case with the low-carbon Fe–Ni welding alloy investigated by Mao et al. [5]. The authors could, however, establish some differences between the two metastable phases by considering the morphologies and by treating the EBSD maps to extract the mean orientation relationship, the average dislocation densities, and the tendencies of variant grouping. Welding alloys needs specific and careful tests in order to take into account the residual stresses. Chen et al. [8] show that, by designing the alloy to reduce the transformation temperature, the martensite volume expansion can offset the usual tensile stresses generated by heat-shrinking; and this reduces the distortion between the welded joints and improves the performances of the welds. As mentioned previously, martensite is not restricted to steels; and other important martensitic materials are shape memory alloys. Li et al. [7] have experimentally investigated the martensitic transformation of Ni<sub>50-x</sub>Ti<sub>50</sub>La<sub>x</sub> alloys (x in the range 0.1 to 0.7). The Ms temperature increases gradually with increasing the La content, mainly because of the decrease of the Ni content in the equi-atomic matrix due to the formation of LaNi and Ti<sub>2</sub>Ni precipitates. Whatever the alloy (steel, NiTi etc.), martensitic transformations share common crystallographic properties, such as the existence of an orientation relationship between the parent and daughter phase, a lattice distortion, a lattice correspondence, a shape deformation, and product variants inherited from symmetries of the parent and daughter phases. The crystallographic theory (PTMC) uses classical matrix notations that require specifying the space of application (direct or reciprocal) and a reference basis. The matrix product (right or left) depends on the space. Gao proposes another notation directly derived from Dirac's brackets. The calculations of lattice transformations, the variants and the compatibility condition are rewritten, independently of any reference basis. Whether or not this notation will be adopted in the future probably depend on its robustness, and its help in avoiding mistakes in the calculations. Even with its 'old' notations, PTMC is mathematically robust and well established. It is a top-down approach that relies on the hypothesis that martensitic transformations result from a 'shear' because the observed shapes of the martensite products are often plates or lenticles. Cayron [9] discusses the origin of this assumption and explains its weakness when the atom 'sizes' are taken into account. He proposes a bottom-up atomistic approach with calculations based on the hard-sphere simplification, with examples for transformations between face-centered cubic, body-centered cubic and hexagonal close packed structures, and deformation twinning. Here again, time will be necessary to compare the two approaches, their simplicity, and their ability to explain the experiments with the minimum of free adjusting parameters.

This Special Issue 'Microstructures and Properties of Martensitic Materials' gives a good overview of some of the experimental and theoretical works made on this domain over the last few years. I hope it will trigger the reader's curiosity and motivate new research into this topic.

Conflicts of Interest: The authors declare no conflicts of interest.

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