

1 billion tons of nanostructure – segregation engineering enables confined transformation effects at lattice defects in steels

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Abstract. The microstructure of complex steels can be manipulated by utilising the interaction between the local mechanical distortions associated with lattice defects, such as dislocations and grain boundaries, and solute components that segregate to them. Phenomenologically these phenomena can be interpreted in terms of the classical Gibbs adsorption isotherm, which states that the total system energy can be reduced by removing solute atoms from the bulk and segregating them at lattice defects. Here we show how this principle can be utilised through appropriate heat treatments not only to enrich lattice defects by solute atoms, but also to further change these decorated regions into confined ordered structural states or even to trigger localized decomposition and phase transformations. This principle, which is based on the interplay between the structure and mechanics of lattice defects on the one hand and the chemistry of the alloy's solute components on the other hand, is referred to as segregation engineering. In this concept solute decoration to specific microstructural traps, viz. lattice defects, is not taken as an undesired effect, but instead seen as a tool for manipulating specific lattice defect structures, compositions and properties that lead to beneficial material behavior. Owing to the fairly well established underlying thermodynamic and kinetic principles, such local decoration and transformation effects can be tuned to proceed in a self-organised manner by adjusting (i) the heat treatment temperatures for matching the desired trapping, transformation or reversion regimes, and (ii) the corresponding timescales for sufficient solute diffusion to the targeted defects. Here we show how this segregation engineering principle can be applied to design self-organized nano- and microstructures in complex steels for improving their mechanical properties.

1. Introduction to the Segregation Engineering principle

The term segregation engineering (SE) describes a self-organized microstructure manipulation method that is based on the combination of (i) confined thermodynamically driven chemical Gibbs segregation via solute decoration to specific lattice defect traps, and (ii) the associated structural, order or phase changes triggered at these decorated sites. The concept of SE works particularly well for steels and Ti alloys owing to their rich spectrum of available allotropic phase transformations [1,2]. Here, we present a number of cases where local solute segregation, and the associated ordering phenomena at lattice defects, lead to confined martensite-to-austenite reversion in Fe-Mn and Fe-C steels.

In these examples the targeted SE effects occur in a spatially confined manner, namely, at lattice defects, which act as efficient and highly thermodynamically attractive solute traps, thus, entailing strong solute segregation when heat treated into regimes that allow for sufficient solute diffusion. The resulting combinations of local strain fields at such lattice defects on the one hand, and the locally altered chemical composition at these defects on the other hand, can initiate structural transitions, solute



ordering, and phase transformation states in such cases where the sample is heated into a phase regime which is intercritical at the decorated and distorted defect region [3,4]. When aiming at the local modification of the microstructure, this SE approach is applied in such a way that these critical conditions are only fulfilled at the lattice defect regions, leaving the adjacent matrix essentially unaffected. These effects, which are essentially built on the decoration driving forces phenomenologically described by the Gibbs adsorption isotherm, are referred to as equilibrium segregation engineering, figure 1 [1].

Alternatively, it is also conceivable to exploit such effects for the case of non-equilibrium compositional gradients that are inherited either from a Scheil-type solidification inhomogeneity or from incomplete intercritical phase dissolution [5-7]. Such scenarios, which are based on kinetically acquired compositional inhomogeneities, are referred to as non-equilibrium segregation engineering. When applying equilibrium SE specifically to grain boundaries we refer to this type of interface manipulation via solute decoration in conjunction with confined ordering or even transformation as 'grain boundary segregation engineering', figure 1 [1].

For creating self-organized microstructures by the SE approach one has to take certain thermodynamic and kinetic rules into account. The thermodynamic rules include the requirement to consider also the competition with the formation of alternative phases in the bulk matrix (rather than being confined to specific defects), the consideration of the equilibrium or non-equilibrium segregation coefficients, co-segregation effects, phase stability (relevant when designing confined states that can undergo spatially confined athermal phase transformations), as well as the interplay of chemical and mechanical driving forces [1-4]. The kinetic rules include consideration of the diffusion coefficients as well as of thermal versus diffusional phase transformation pathways [5-7].

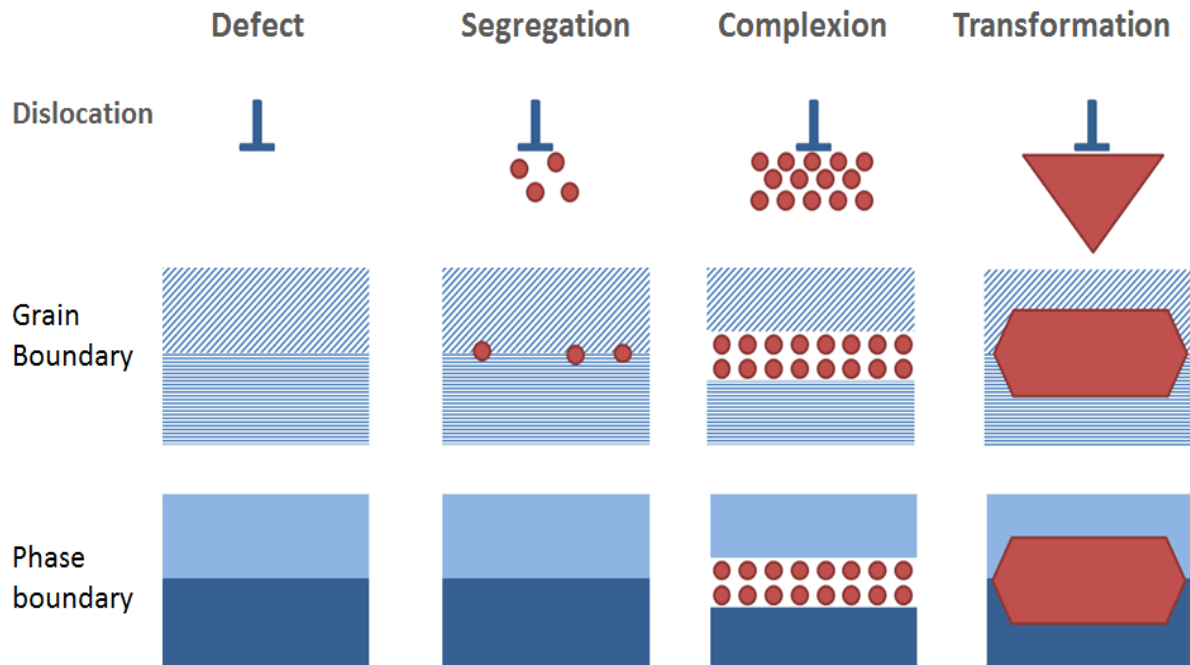


Figure 1. Some of the decoration and ordering states utilized at lattice defects in the field of SE. The chemo-mechanical interactions promoting solute decoration of lattice defects allow, through adequate heat treatment, to manipulate the structure and composition of the defect sites. This can lead to either conventional Gibbs equilibrium solute segregation, lowering the defect's self-energy, complexion or similar defect stabilized confined structure formation or even confined phase formation and transformation

The main idea behind the SE concept lies in the approach to consider solute decoration to defects not just as an undesired side effect associated with processing and heat treatment but to exploit it as a tool for the site-specific manipulation of interfaces with the aim to stabilize small grain sizes or to create intrinsically organized nano- or microstructures consisting of the initial matrix phase and segregation-induced ordered or transformation phase regions that can be rendered to follow the template of the landscape of the lattice defect structure, figure 2 [1].

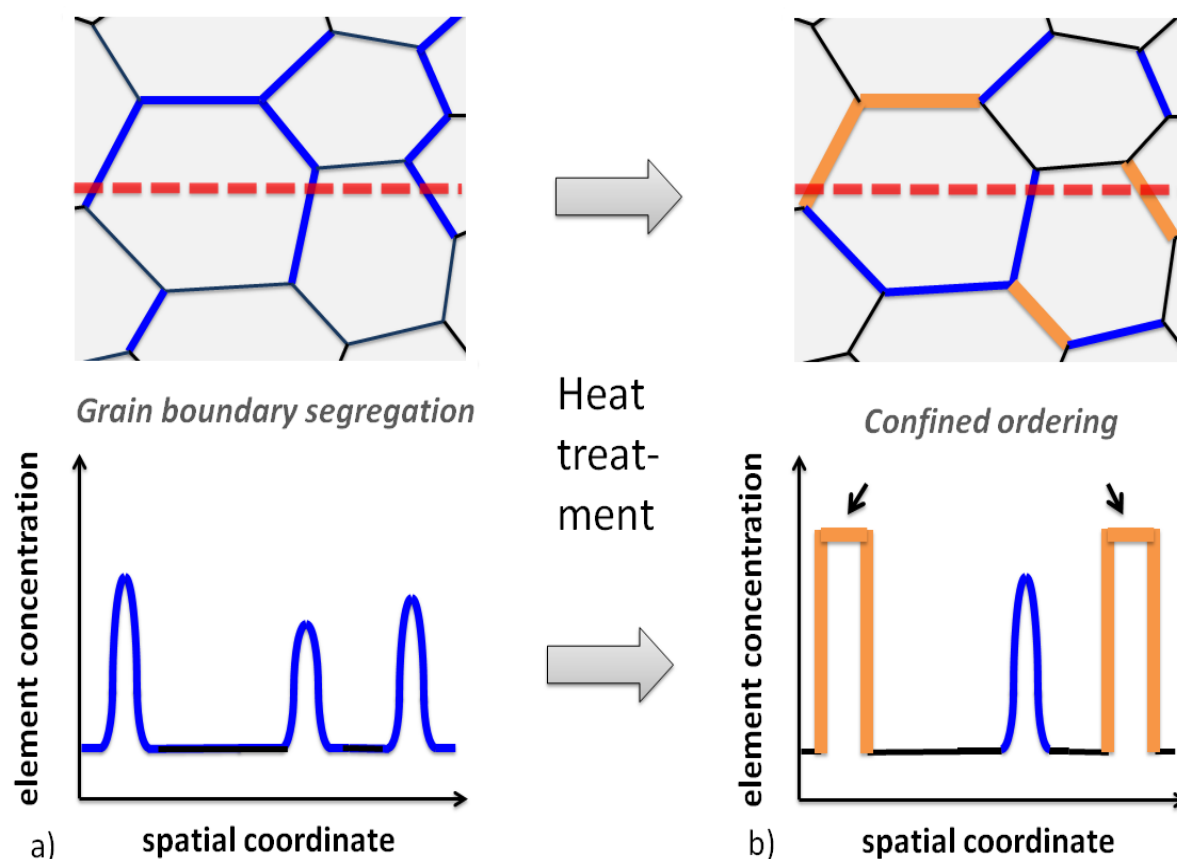


Figure 2. Example of grain boundary SE. Solute segregation to grain boundaries can, upon heat treatment, lead to phase transformation. The change in chemical composition, together with elastic distortions at interfaces, can be used for instance to create reversed austenite in a martensitic matrix.

2. Probing grain boundary segregation by correlative atom probe tomography and electron microscopy

The systematic manipulation of lattice defects through their trapping effect on solutes and associated means of modifying them in terms of confined ordering or transformation effects requires characterization methods that are suited to probe such phenomena at sufficiently high chemical, spatial and crystallographic resolution [3,8-13]. Such correlative characterization of lattice defects can be achieved by the use of atom probe tomography in concert with scanning electron microscopy, scanning transmission electron microscopy and/or transmission electron microscopy (TEM) [1,8,11].

Atom probe tomography enables revealing local solute decoration at defects with near ppm precision. Electron microscopy methods, with their different resolution features regarding imaging and diffraction, provide the required additional corresponding structure resolution to analyse these sites, figure 3. Practically all electron microscopy probing methods can nowadays be applied directly to atom probe

tips, including high resolution atomic column imaging in corrected scanning transmission electron microscopy.

Hence, by (i) preparing atom probe tips via site specific focussed ion beam cutting, (ii) imaging and diffraction of these tips in electron microscope studies, and (iii) the final evaporation and compositional probing of the so characterized tips in the atom probe, a joint and fully correlative analysis of solute decorated or ordered states at lattice defects down to the atomic scale is enabled, figure 4 [3,8,9].

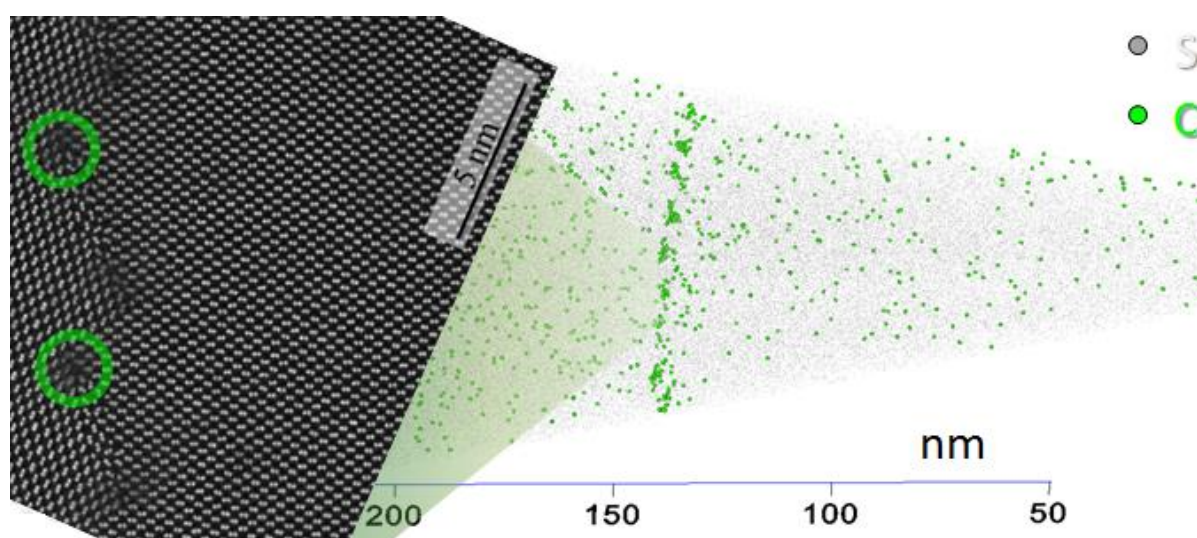


Figure 3. Correlative electron microscopy and atom probe tomography of grain boundary segregation in Si. Taken from the work of Stoffers et al. [13,14].

Figure 4 shows an example where Mn is strongly segregated to dislocations and grain boundaries. The Mn concentration of the Fe-Mn alloy has been mapped using correlated atom probe tomography in conjunction with TEM imaging conducted directly on the atom probe tip. Such measurements are capable of quantitatively revealing the extent of solid segregation at defects such as dislocations and grain boundaries [3].

Interestingly, one can observe in figure 4 that some of the dislocations that are clearly visible in the TEM image do not appear in the atom probe tomographic analysis in terms of any solute concentration envelope, indicating that these dislocations are obviously not sufficiently solute decorated. In contrast, some of the dislocations that are highlighted in the atom probe tomographic analysis as a result of their local concentration enrichment are not observed in the TEM images, since the diffraction condition is not fulfilled locally, i.e. more beam conditions would need to be used for the full characterization of these dislocations.

The specimen from which these atom probe tomography tips were cut by using site specific extraction by focused ion beam instrument was a 50% cold rolled and subsequently 450°C/6h heat-treated Fe-9wt.%Mn model alloy. The data shown in figure 4 are taken from the work of Kuzmina et al. [3].

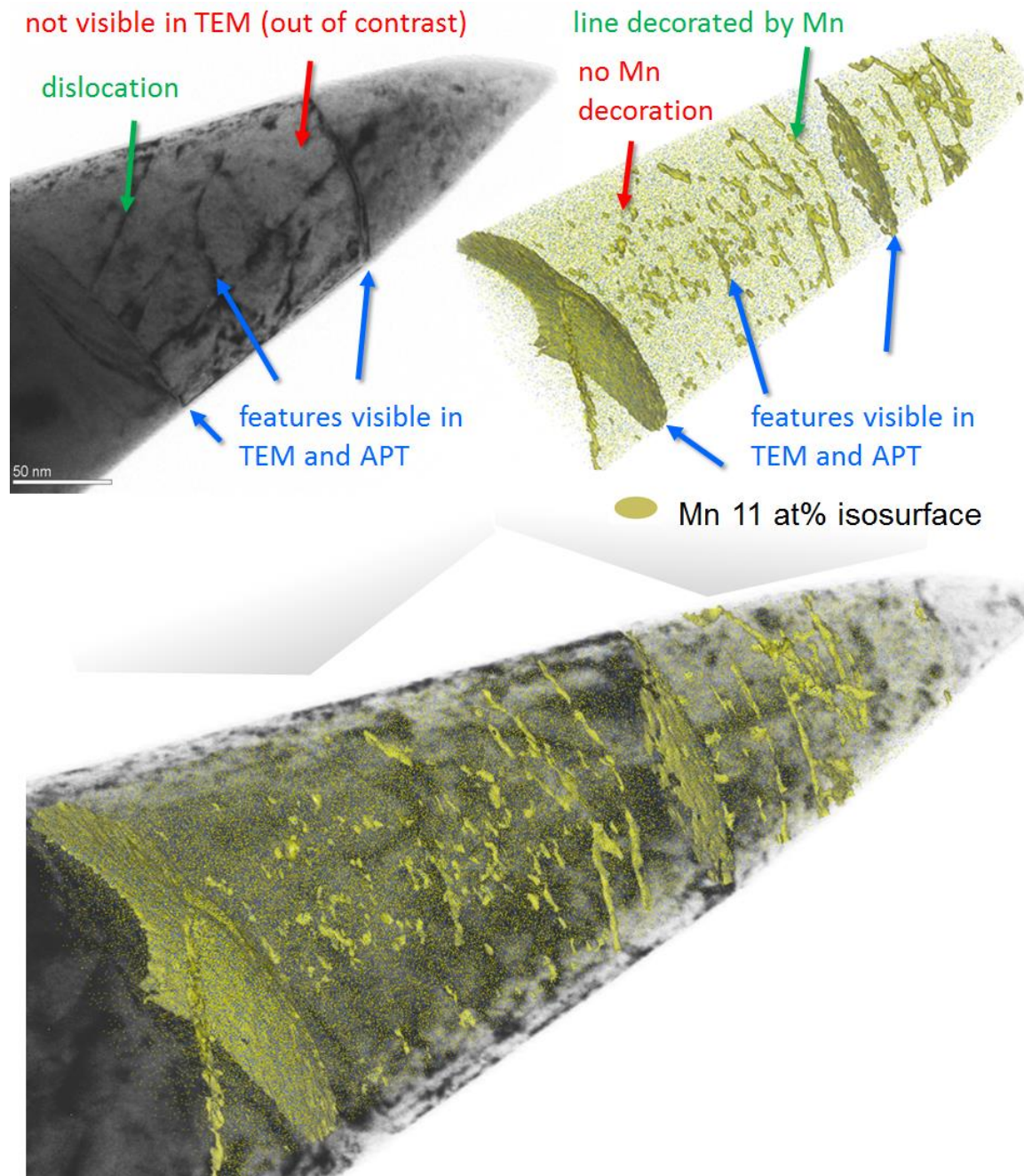


Figure 4. Mn concentration in a Fe-Mn alloy mapped using correlated atom probe tomography in conjunction with TEM imaging conducted directly on the atom probe tip. The data and some of the images are taken from [3].

3. Confined martensite-to-austenite reversion at lath interfaces creates self-organized two-phase nano-laminates

SE can be used for the self-organized design of two-phase or even multi-phase laminate microstructures. For this purpose we selected a steel with 9 wt.% Mn, owing to the high segregation tendency of Mn to lattice defects in Fe. After first heating the alloy into the solid solution austenitic regime, the material was subsequently quenched into the cubic martensite state. After this the steel was finally intercritically heat-treated at 600° C for 8 hours, figure 5.

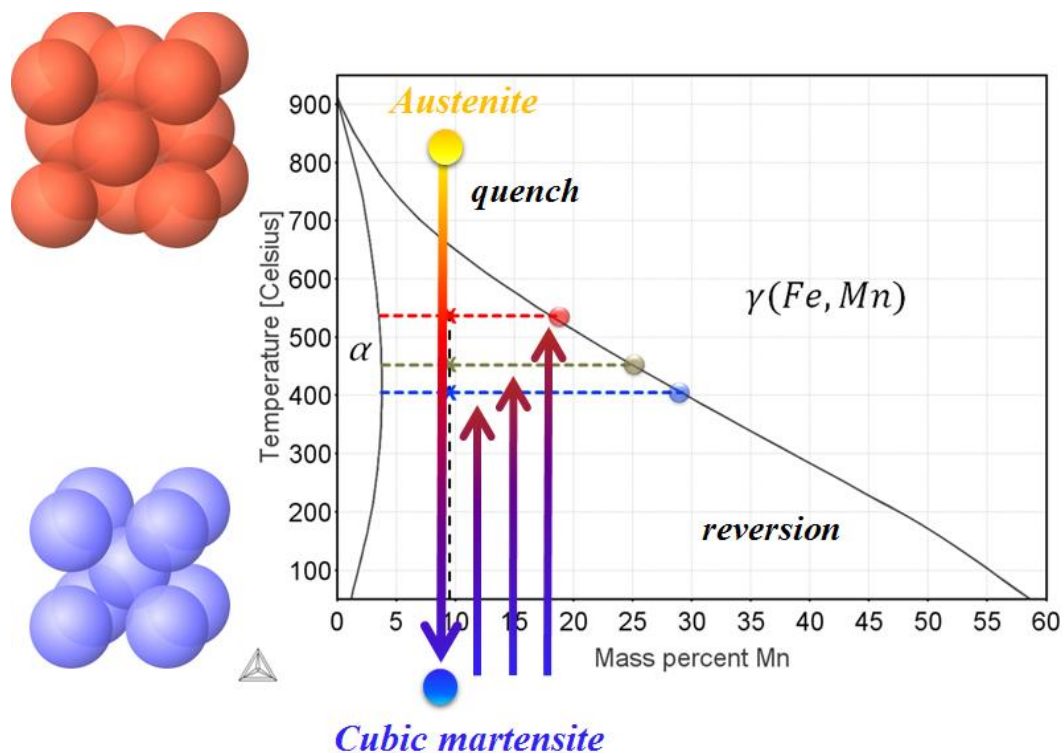


Figure 5. Martensite-to-austenite reversion heat treatment [1,3,4].

During this re-heating treatment the martensite lath grain boundaries, which formed during quenching, were gradually decorated by Mn following the Gibbs adsorption isotherm. At these decorated interfaces martensite-to-austenite reversion was observed owing to the chemical decoration in conjunction with the local elastic distortion. This process occurred in a very confined manner, leading to transformation of at first only the interface regions, figure 6 [15-17]. With further heat treatment these originally confined and only nm-thin martensite-to-austenite transformation zones at the former lath interfaces could be grown further, expanding and thickening sideways into the adjacent martensite matrix [15-19].

Next it was studied how such martensite – austenite nano-laminate steels can lead to improved mechanical properties such as high damage resistance, figure 7,8. These laminate microstructures were found to efficiently share the load by dynamic strain partitioning among the lamellar arranged phases, specifically when one of the phases undergoes load-driven phase transformation, such as the metastable austenite in the case shown in figure 6. The specific thermodynamic stability of the austenite laminates can be designed through the appropriate partitioning during heat treatment.

Recent experiments have also shown that such nano-laminate steels can exhibit increased crack resistance, particularly in such cases where one of the laminate phases, such as the austenite, is rendered metastable so that it can deform via a transformation induced plasticity (TRIP) effect when mechanically loaded [20]. Mechanical fatigue of complex engineering alloys is an ubiquitous phenomenon and it is often dealt with by simply including high safety-factors in structural design solutions. In a nano-laminate Fe9Mn3Ni1.5Al steel (in wt.%) we found the simultaneous activation of roughness-induced and of transformation-induced crack termination mechanisms [21].

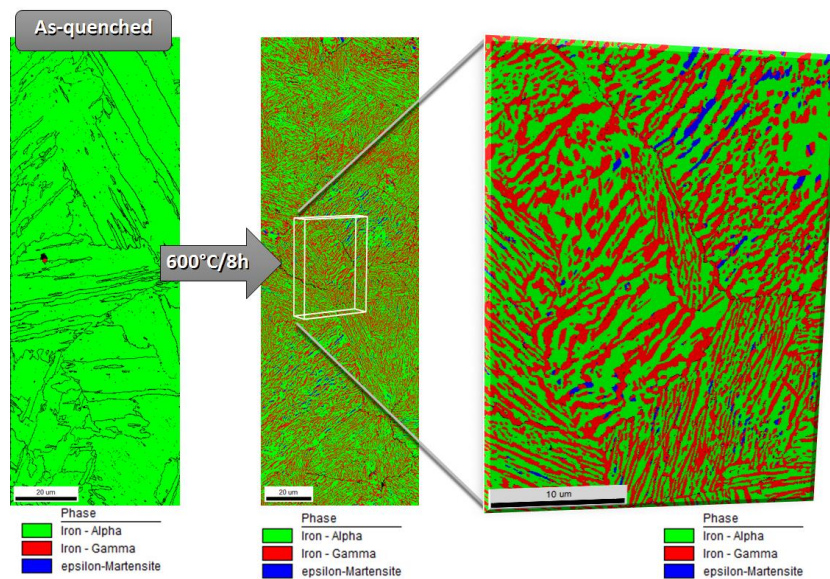


Figure 6. Example of a martensite-to-austenite reversion heat treatment. The EBSD map shows how the lath interface segregation in concert with a spatially confined martensite-to-austenite phase transformation has been used for the design of a laminate steel consisting of three phases. The process proceeds through a segregation plus reversion heat treatment after the initial quench from the austenite solid solution regime. The lamellar arrangement of the newly formed transformation microstructure is due to the fact that the Mn segregated to the martensite lath interfaces, entailing site-specific austenite reversion at these interfaces. The data and EBSD maps are taken from the work of Wang et al. [15-18].

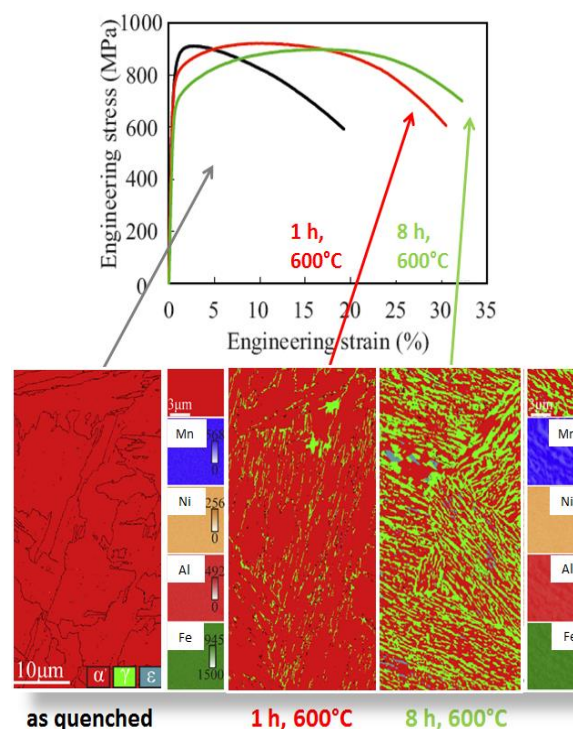


Figure 7. Example of the improvement of the stress-strain response of the laminate steel. The data are taken from the work of Wang et al. [15-18].

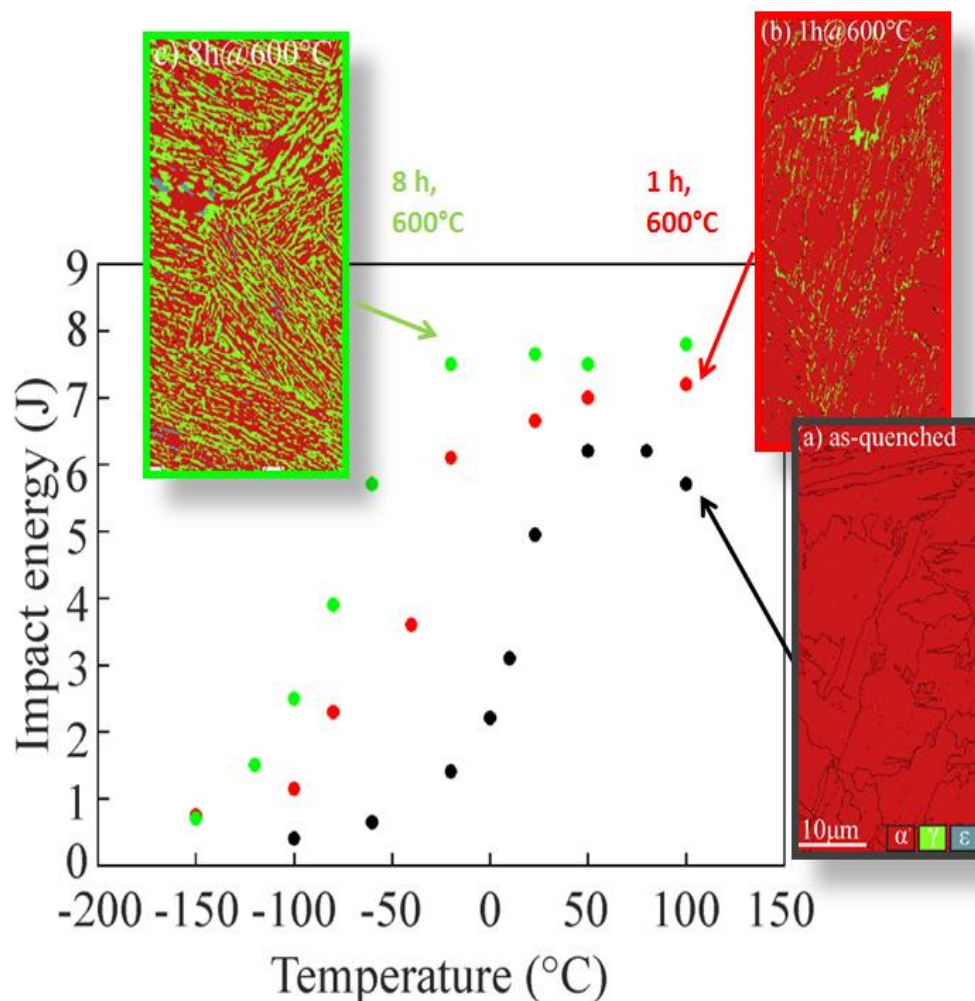


Figure 8. Example of the improvement in the impact toughness response of the laminate steel. The data are taken from the work of Wang et al. [15-18].

The alloy consists of a hierarchical structure comparable to bone, composed of laminate-arranged martensite and metastable austenite phases, and showed improved fatigue resistance compared to conventional high strength alloys as for example DP steels [21-23]. The formation of localized compressive stress fields, which were created from the volume-expanding deformation-induced phase transformation from the metastable face centered cubic γ phase into the near body centered cubic α' -martensite at crack tips, was observed to suppress crack nucleation and crack propagation, figure 9 [24].

4. Non-equilibrium segregation engineering through vessel phases: Tailored austenite retention around partially dissolved precipitates

Another approach to the utilization of confined transformation zones consists in the deliberate introduction of site specific and geometrically confined non-equilibrium segregation zones. This microstructure design method is based on the utilization of so-called vessel phases, which were recently introduced and applied to the design of austenite in multiphase steel microstructures [5-7,25],

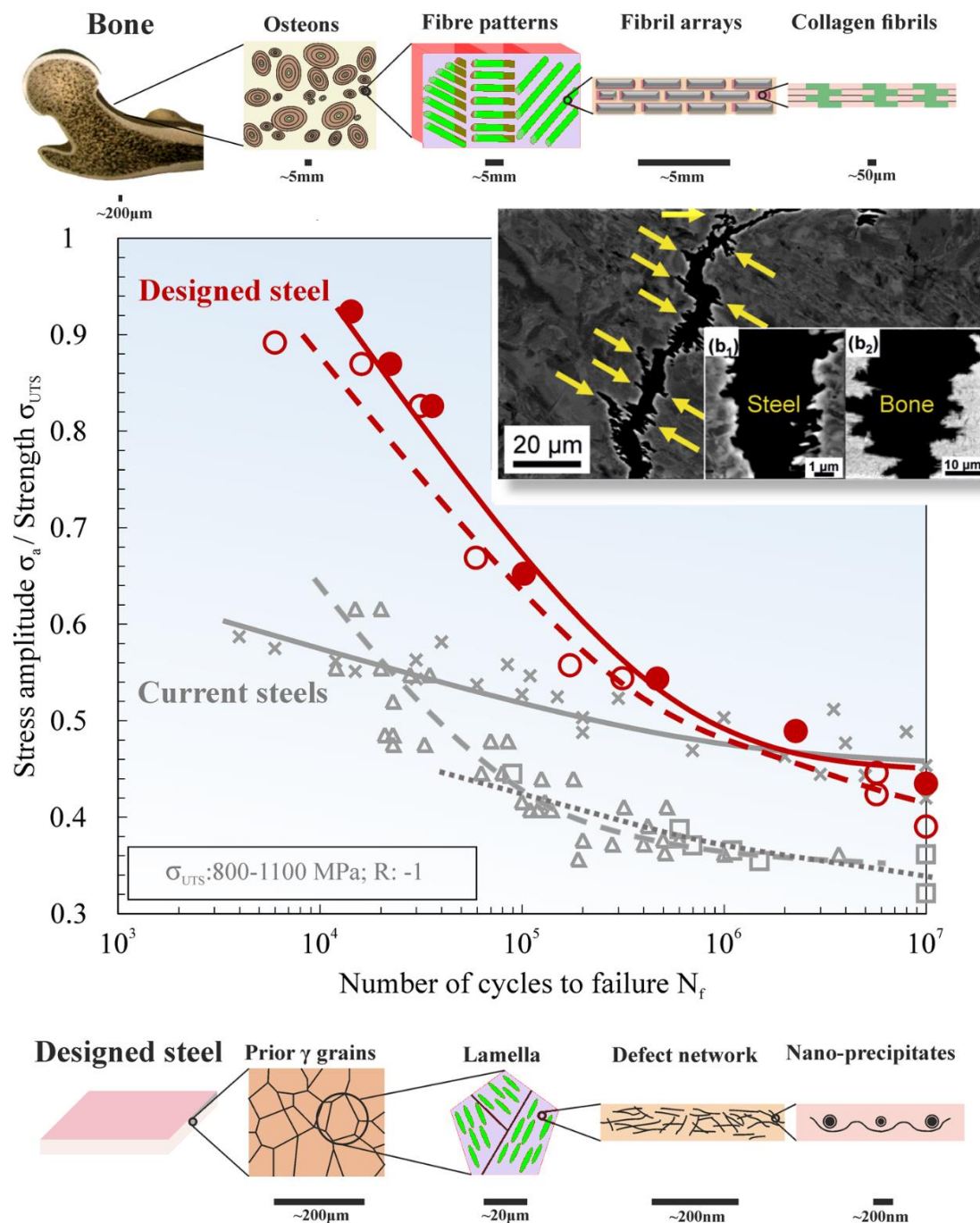


Figure 9. Bone like fatigue resistance observed in a nano-laminate martensite-austenite steel. The figures and data have been taken from the work of Koyama et al. [24].

figure 10, 11. Vessel phases are precipitations carrying certain elements that can – upon partial or complete dissolution – be released to create well defined local phase states, such as metastable austenite at those positions where these precipitates were originally located.

In complete equilibrium the confinement of these localized diffusion regions around the dissolving particles would be lost owing to far reaching diffusion. In the non-equilibrium case, however, this diffusion process toward equilibration is interrupted, so that confined regions with a composition

different from the composition of the matrix can be formed.

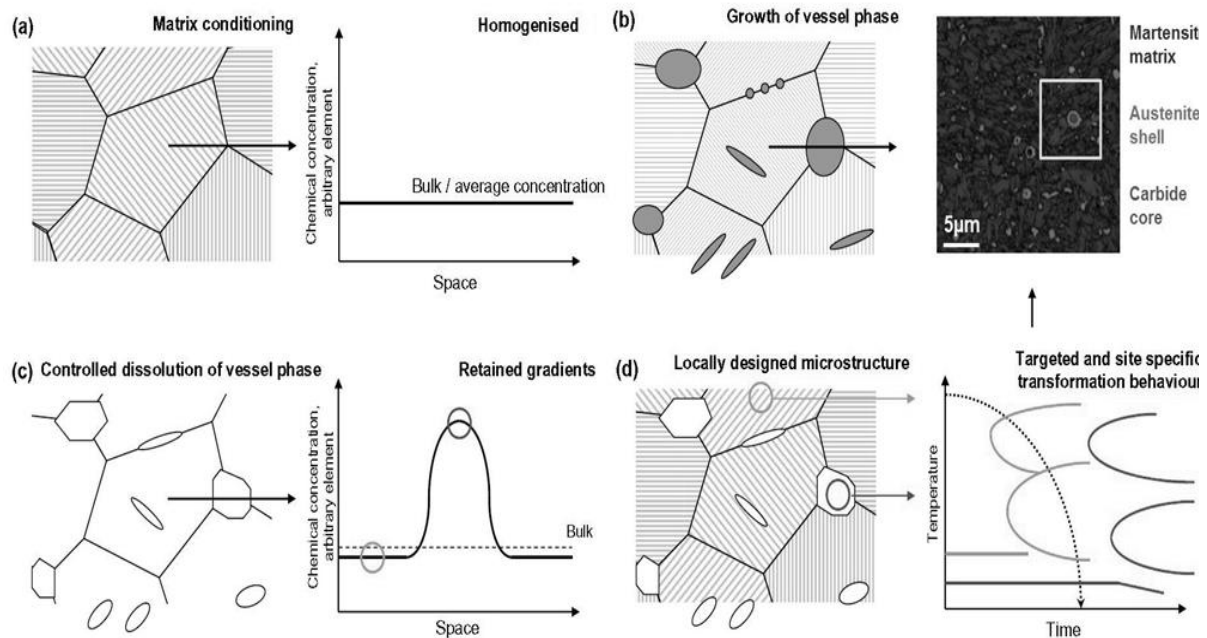


Figure 10. Schematic of site-specific phase transformations induced by use of vessel phases. These phases are precipitates that exhibit a high equilibrium enrichment factor before being made to dissolve upon heat treatment, creating local retained austenitic zones within an otherwise martensitic matrix upon quenching. The size and stability of these austenitic zones can be adjusted by tuning the diffusional fluxes during the dissolution treatment. The figure has been adapted from Belde et al. [5-7,25].

The approach consists of three main processing steps. The first step in this sequence is conducting an adequate tempering cycle to achieve sufficiently high compositional homogeneity of the matrix. This processing step is also referred to as the matrix conditioning step, as it is used to control the precipitation conditions of the vessel phase. The second processing step is a heat treatment for conducting the vessel phase precipitation. This step is termed the accumulation step, as it serves to build up high enrichment factors with respect to the bulk material. It is essential in this approach as the imposed temperature and time define the composition and stability of the precipitates that act as elemental containers to later provide the elements that help creating the confined metastable phase region upon dissolution.

The third step is the complete or incomplete vessel phase dissolution, referred to as the dissolution step. Controlling the vessel phase dispersion and morphology allows one to design retained austenite regions by using the site-specific chemical gradients that form around the dissolving vessel phases to induce a local reduction in the martensite start temperature.

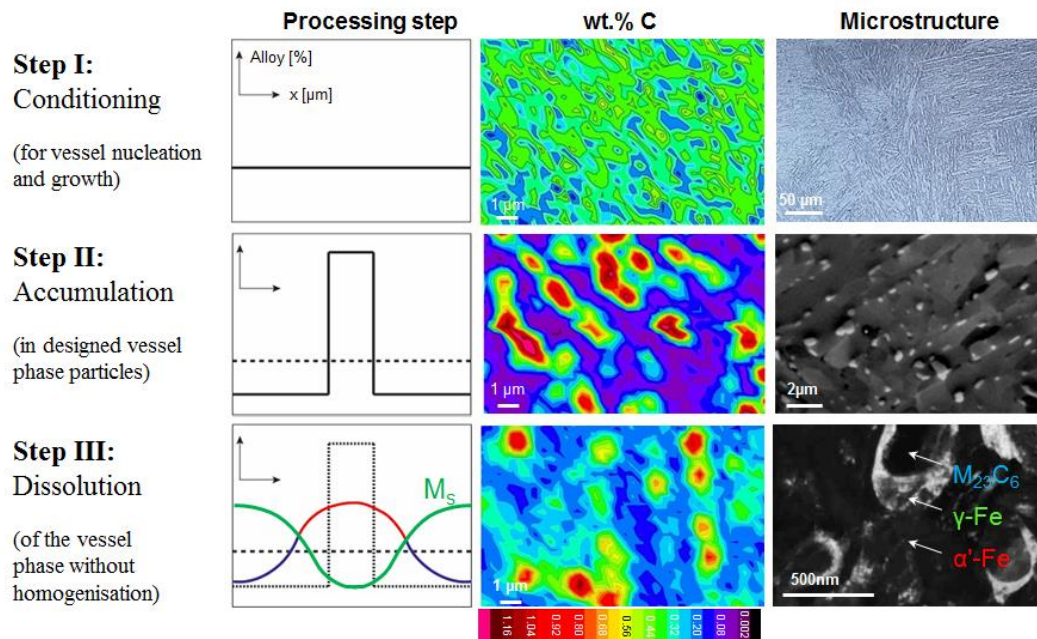


Figure 11. The three phases of vessel segregation engineering in schematic, chemical, and microstructural representations; adapted from the work of Belde et al [5-7,25].

5. Conclusions

In this contribution we have shown how the site specific equilibrium or non-equilibrium solute decoration of lattice defect traps, such as dislocations and grain boundaries, can be used to tune the microstructure by the development of confined regions with different composition, structure, phase state and / or stability within otherwise homogeneous microstructural landscapes.

Because the spatial arrangement of the used trapping pattern agents, viz., the distribution of the dislocations and grain boundaries, is often characterized by small average defect spacing (such the dislocation spacing, and the spacing between lath grain boundaries), SE allows self-organized structuring to be achieved at very small length scales.

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