

“Second phases” in steel: a review of the concept, origin, and their relevance for properties

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Abstract

Steels are multiphase alloys with an increasingly complex constitution. This complexity of steel microstructures has been recognized since the birth of steel physical metallurgy. Non-metallic inclusions have also been very early recognized as relevant to the understanding of steel behavior. With the advances in precipitation hardening and grain size control, many precipitate phases gained importance in steel design. Around 1950-70 the term “second phases” was coined as an all-encompassing definition that would cover non-metallic inclusions as well as fine precipitates such as nitrides and carbonitrides even in steels that already had a multi-phase constitution. While this classification may be practical in some cases, we argue that it hinders the proper understanding of the origin and effects of particles in steel and unduly complicates the understanding of the phenomena in which they take part. In this work, we briefly review the origin of the second phase particle concept and discuss the critical properties of particles with respect to their influence on steel behavior. Through several examples, we propose that size and volume fraction are the main variables in evaluating how particles affect steels. While chemical composition is key to understanding the origin of the particles, we suggest that these variables are, together with interface properties, the most relevant to understand the effect of particles on steel behavior.

Keywords: Steels; Non-metallic inclusions; Grain size; Precipitation; Austenite.

1 Introduction

Steels are multiphase alloys with an increasingly complex constitution. This complexity of steel microstructures has been recognized since the birth of steel physical metallurgy [1,2]. Furthermore, the origin and relevance of non-metallic inclusions [3,4] has been highlighted both by “chemical” and physical metallurgists [2] since the development of a more scientific understanding of steels [5,6]. The discovery of precipitation hardening in aluminum alloys [7] lead to the use of the expression “second phases” in the 1930’s [8] and soon not only non-metallic inclusions but also particles that cause “obstructions” to grain growth [9,10] were being grouped as “second phases” in steel, in a somewhat arbitrary, if not confusing way. By 1959 Edelson and Baldwin [11] were deliberately creating composite materials with a metallic matrix to investigate “*the effect of second phases on the mechanical properties of alloys*”. By 1971 the term was well established in steel metallurgy and a series of meetings were started under this classification, addressing the effects of precipitation hardening, non-metallic inclusions and other “particles” [12] on the properties of steel [13]. In his excellent review on “Alloy Design using second phases” Decker addresses [14] a large number of properties that can be affected by second phases. Albeit he does not present a clear definition of “second phases” he lists several carbides, oxides, nitrides, intermetallics and metal phases that can have importance in the design of metals containing particles and

emphasizes the importance of their volume fraction, size, and properties (including bonding to the matrix and atomic ordering). As a measure of their importance, Decker mentions that the world has produced, in that year, around 16Mt of cementite as second phase in steels! The attempt to define “second phase particles in steel” by Bandi [15:136] sheds light on the complexity of this all-encompassing concept.

[The approximately 35 elements used as alloying elements in steels] [...] often change the mechanical properties of the steel by combining with oxygen, nitrogen, carbon, or sulfur to form precipitates... that are referred to as second phase compounds. Sometimes [these]... will contain two metals ..., but most often the second phases are oxides, nitrides, carbides, sulfides, carbonitrides, carbosulfides, and similar compounds. These compounds may be formed in the molten bath, during solidification, during rolling or forming, during heat treatment, and sometimes even during storage at ambient temperature.

This all-encompassing definition has not been very helpful to most steel engineers who struggle to understand the different effects of different particles and when to name them precipitates, non-metallic-inclusions or “second phases” in a steel with many phases present

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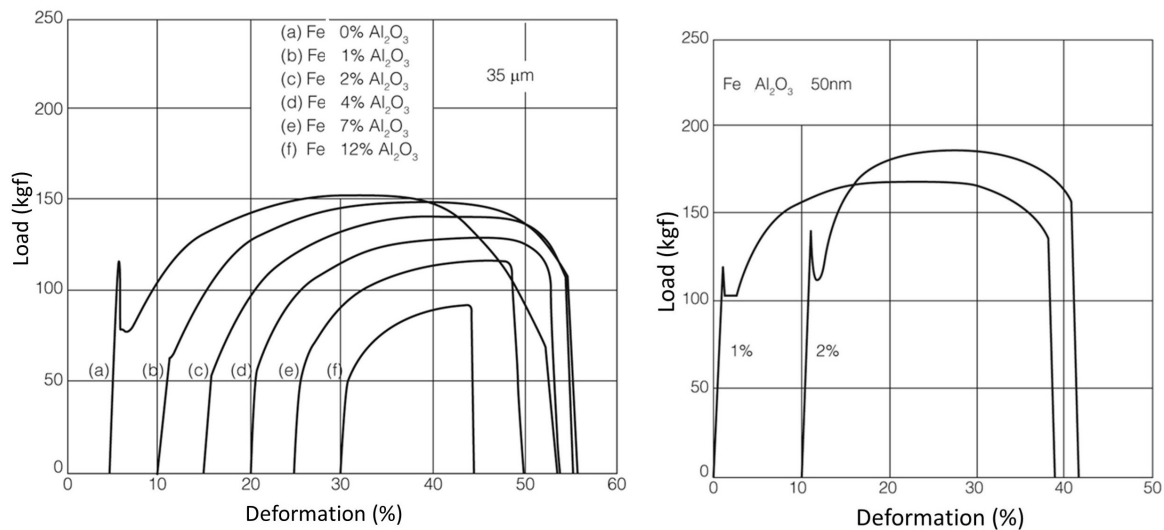


Figure 1. The effect of a dispersion of spherical alumina particles in sintered iron. (a) Larger particles (35 μm) cause the results expected from a composite material while; (b) smaller particles (50 nm) cause dispersion or “precipitation” hardening. Adapted from [18].

in its microstructure. The objective of this work is not to contest the well-established terminology but to attempt to review relevant work that shows the main criteria that help define how a particle will influence the properties of the steel multi-phase matrix. This hopefully will provide guidance to steel metallurgists in better understanding the effect of these particles and improve their ability to perform better alloy design.

2 Properties relevant to the interaction of “second phases” with a matrix

Macroscopic second phases are used in composite materials since the Mesopotamian and Egyptian civilization [16]. Albeit many concepts are important in composite design, second phases volume fraction, shape, size and properties as well as interface properties are critical to understand the effects of these phases on the resulting composite material (e.g., Refs [16,17]). The understanding of the effect of microscopic second phases in metals has evolved in the last century, however. The difficulties associated with characterization of the particles have certainly played an important role in delaying this understanding. It is also well established now that the same factors listed above are relevant to the effect of these particles in metals. In the microscopical scale, crystal structure and the possibility of interfacial coherence add a further layer of complexity to the theme. Figure 1 presents the effect of macro and microscopic additions of alumina to steel. One evident issue is how to define a boundary between macro and microscopic particles in different base materials or metals.

When one looks at the volume fraction and size of “typical” second phase particles in steels, different families of “second phase” particles are evident (Figure 2).

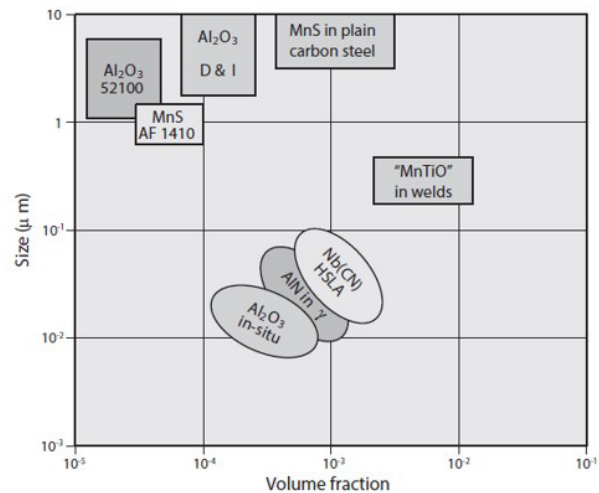


Figure 2. Volume fraction and size for typical second phase particles in steels. Nonmetallic inclusions normally have a combination of size and distribution out of the region where second phase hardening or austenitic grain size control can be achieved. This region is indicated by the range where one finds the niobium carbonitrides Nb(C,N) in HSLA steels, aluminum nitride (AlN) in engineering steels, and the results of a synthetic dispersion of alumina in steel (indicated in the figure as Al₂O₃ in situ) that resulted in effective austenitic grain size control. Adapted from [19]. Data from [20-29].

Thus, it seems that a reasonable approach may be to initially avoid the distinction between chemical composition and focus on size and volume fraction of second phases in steel, in order to understand their effect on the steel behavior. The “macro and micro” terminology is already used for non-metallic inclusions (e.g., Refs [3,30,31]). To avoid confusion, we will separate into larger and smaller particles, keeping in mind that the limiting size in this somewhat arbitrary classification will depend on the properties of the steel “matrix” as those of the second phase.

3 Larger particles

Large second-phase particles in steel include, in general non-metallic inclusions, carbides (such as cementite) in normalized and annealed steels, and martensite “islands” in dual-phase (DP) and in multi-phase (MP) steels.

Non-metallic inclusions can be deformed during hot work, complicating the issue of shape and introducing anisotropy [3,4]. The same happens with carbides in cold worked steels. In hot worked or heat-treated steels carbides and martensite have shapes that are mostly dependent on the shapes defined by transformations following thermomechanical treatment. Primary carbides, however, break and redistribute during thermomechanical treatment and, like non-metallic inclusions, will have shapes and distribution associated with these phenomena [19].

Although non-metallic inclusions may be produced in sizes small enough to affect the material in other ways (see Figure 1 and item 4) they are normally large enough to lose coherency to the matrix and to have relatively weak bonding to the steel matrix. These particles have a large effect on the properties related to ductile fracture (ductility, toughness and reductions of area being the most common) and fatigue initiation, and on the anisotropy of these properties. (For a more complete discussion see Ref [4].).

In most cases the cross section of the inclusions on the mechanically loaded section is the critical feature, for a given size and volume fraction (Figure 3 and Figure 4).

This leads to ingenious solutions of problems in many steels. Both tire cord and spring steels, for instance, are engineered to minimize the cross section of inclusions in the transverse section using inclusions that are readily deformed in the longitudinal direction of the wire during hot working.

Both the inclusion plasticity concept developed by Kiessling (Figure 5) as well as the proper care to avoid inclusion crystallization and hence loss of plasticity [34] are essential and inclusion engineering, starting at the melt shop, play a paramount role in the process [35-37].

In the case of fatigue, for instance, size of a discontinuity is the paramount parameter, and it may be either a “larger” particle (non-metallic inclusion or bainite island) or an artificial defect, as has been thoroughly demonstrated by Murakami and collaborators (e.g., Refs [33,38,39]). Of particular interest were the tests performed by Murakami and co-workers [40] with super-clean bearing steel (electron beam remelted). In this steel, with total oxygen content of 4 ppm, fatigue failure did not originate on non-metallic inclusions, but rather in microstructural inhomogeneities, small volumes of bainite (HV=560) instead of martensite (HV=770). During microstructural investigation they have clearly demonstrated that bainite islands of average dimension of $\sqrt{\text{area}} = 15.7 \mu\text{m}$ were the initiation sites for fatigue fracture. These islands were larger than the non-metallic inclusions in the super clean steel as shown in Figure 6.

The effect of large carbides in steel has been thoroughly studied in the end of last century and the behavior approaches closely that of a ferrite-cementite composite, albeit some deviations mostly due to deformation constrains are observed (see Figure 7, for instance). Ashby et al. [42] have investigated the effects of constrains caused by the interfacial strength in a brittle matrix (glass)- ductile reinforcement (lead). They demonstrated that toughening by the lead reinforcement only happened when the lead-glass interface was weakened, so that the lead wire could debond and then fully deform plastically, reaching necking. If bonding was strong, necking was prevented and there was no effective toughening. This is probably somewhat similar to what Butler and Drucker [43]

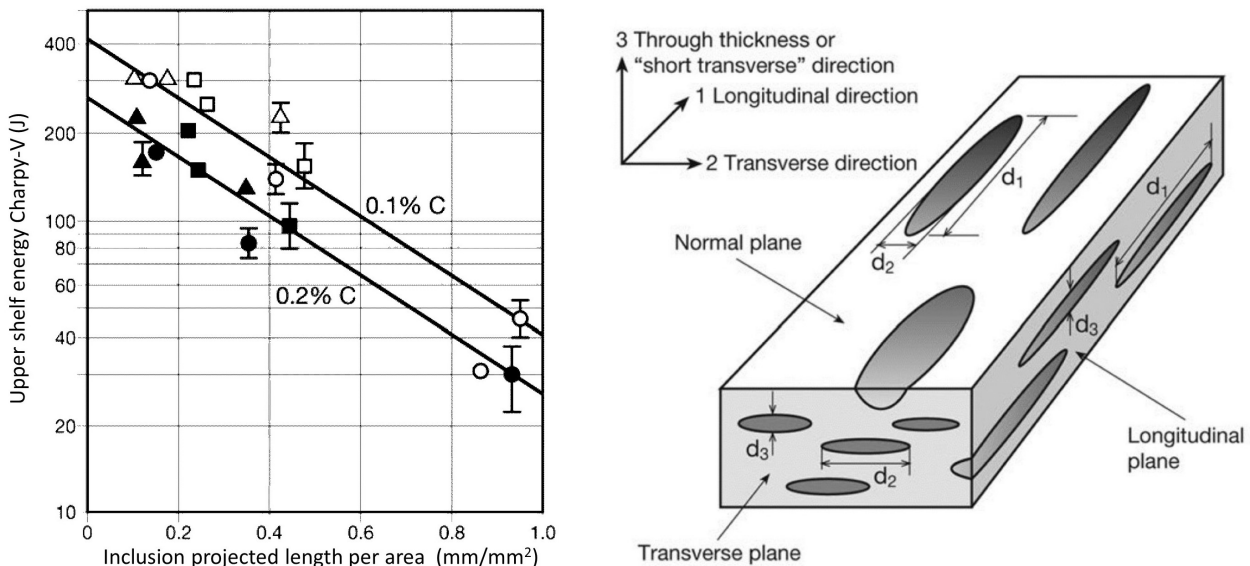


Figure 3. (a) Effect of the inclusion projected length (or size in the loaded cross section) on the tested area on the energy absorbed in the upper shelf of Charpy-V impact tests for a C-Mn structural steel for different specimen orientations; (b) Nomenclature adopted for planes and directions used in the characterization shown in (a). Data obtained with sulfides. Adapted from [32].

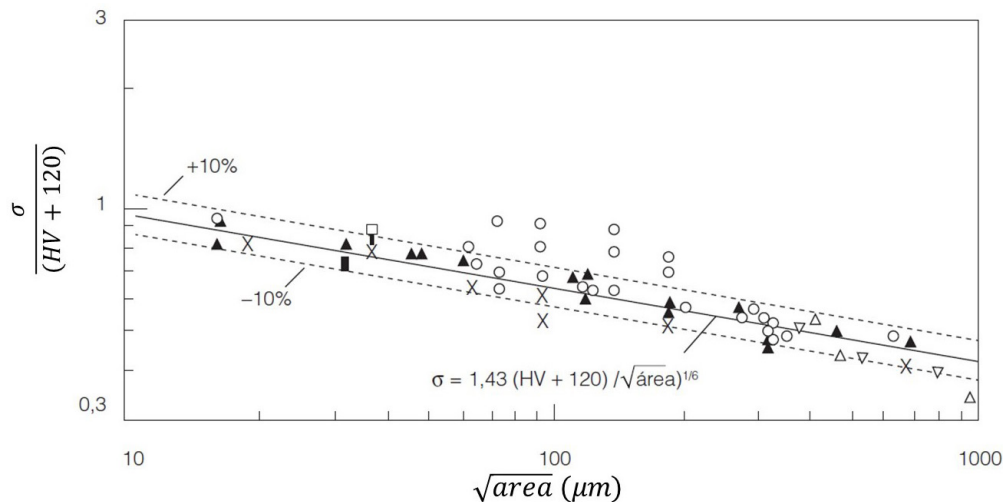


Figure 4. Relationship between $\sigma_w/(Hv+120)$ and $\sqrt{\text{area}}$ where “area” is the area of the inclusion transverse to loading, causing failure in rotating bending fatigue tests. The graph confirms Murakami’s equation, at the bottom of the figure. Adapted from [33].

observed in ferrite-carbide structures, where cementite can constrain ferrite deformation [44] in a complex deformation and fracture process [45-47].

The ductility of DP and MP steels is critical to many applications, in special in respect to formability. Detailed microscopic evaluation of the deformation process supported the development of macroscopic models to describe the behavior of DP and MP steels well into the plastic region (e.g., Refs [48-50]). Tasan et al. [50] mapped the damage mechanism observed by various authors during deformation of DP steels. As ductile fracture happens by microvoid coalescence also in these steels, these damage mechanisms are critical in the control of their ductility and formability. When martensite areas are present, it is very difficult to properly couple hard martensite and soft ferrite deformation and interesting damage mechanisms become operative. In the lower volume fraction region of Figure 8 martensite can be understood as a “larger” second phase in the DP steel matrix. Observations of the damage process indicate that lower deformations should be required to nucleate voids at inclusions than at ferrite-martensite interfaces. The first description of these effects in DP steels, in a semi-quantitative way, was presented by Marder [51].

Due to the novelty of the mechanisms of martensite cracking or ferrite-martensite debonding in DP and MP steels observed in the XXI century, many authors have overlooked the classical and important effect of non-metallic inclusions on the ductility of these steels, in special since they are, in general, processed through clean steel routes to optimize ductility. Jamwal et al. [52] performed careful fractographic analysis of DP980 steel and noticed that the effect of non-metallic inclusions was present, but, since the steel was very clean, the most important factor in the decrease of ductility were the martensite-ferrite pullouts, points in which there was void initiation either due to debonding or cracking, as presented in Figure 9. This is in general agreement with the observations in Figure 8. Heibel et al. [48]

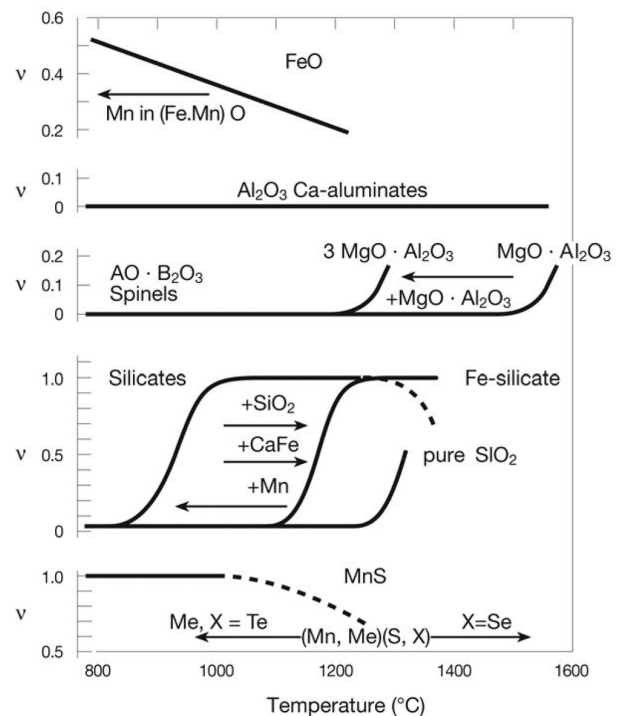


Figure 5. The influence of temperature on the relative plasticity of various typical nonmetallic inclusions in steels. Relative plasticity v is measured as $v = \text{nonmetallic inclusion plasticity/steel plasticity}$. Adapted from [31].

observed that non-metallic inclusions initiated voids earlier in the deformation process than the cracking or debonding of martensite. Thus, non-metallic inclusions led to larger voids. In a clean steel, the author observed that the effect of non-metallic inclusions should be less pronounced than the nucleation of voids associated with martensite [48] in agreement with the quantitative observations of Jamwal et al. The processes occurring during ductile fracture have been

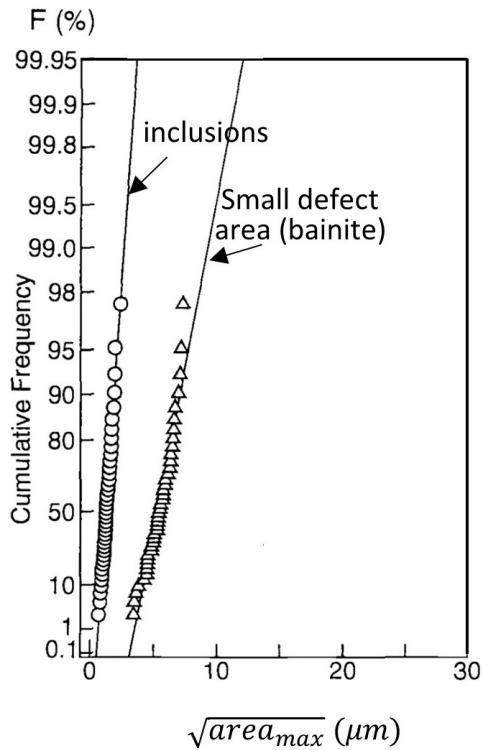


Figure 6. Cumulative frequency distribution of $\sqrt{\text{area}_{\text{max}}}$ of inclusions and bainite islands in superclean EB remelted bearing steel. For details about the measuring technique see [41] and appendix A to Ref [33]. Adapted from [40].

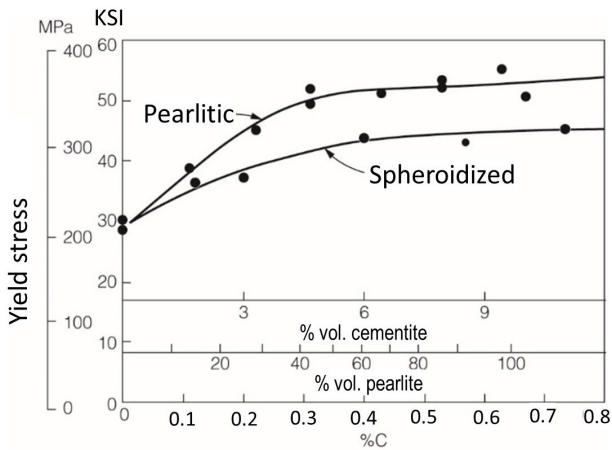


Figure 7. Yield strength of carbon steels in which the ferritic grain size was kept approximately constant at (ASTM \cong 8) as a function of pearlite and cementite volume fraction as well as carbon content. The lines follow approximately a simple composite strength model in which the constraint of ferrite plasticity by the rigid cementite is taken in consideration. Adapted from [43].

modeled by LeRoy and coworkers [53]. This relatively simple model makes possible estimates of matrix-particle strength which are important in many cases, such as the behavior of DP and CP steels [54-56]. These processes have been modeled with increased precision, as reviewed by Benzerga and collaborators [57,58].

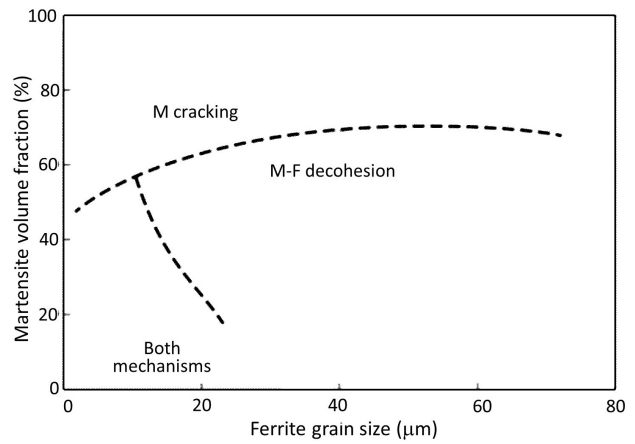


Figure 8. Operating damage mechanisms in DP steels as a function of martensite volume fraction and ferritic grain size. Martensite cracking and ferrite-martensite decohesion (or debonding) are the prevalent mechanisms. Compiled by Tasan and co-workers, adapted from [50].

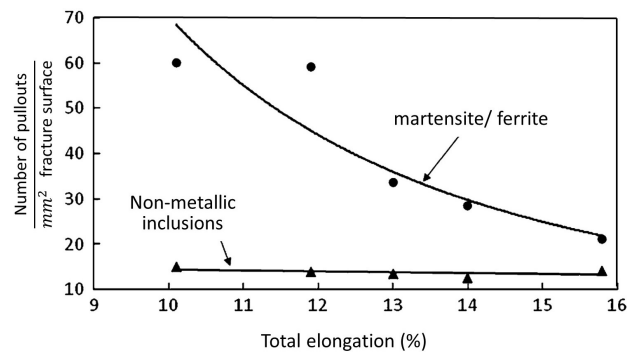


Figure 9. Number of pull-outs per mm^2 of surface area as a function of total elongation in tensile test. DP980 steel. Adapted from [52].

4 Smaller particles

As particle size is reduced, second phases can interact in other ways with the steel matrix. When particles are sufficiently small, they may interact with grain boundaries and/or with dislocations.

As a rule, non-metallic inclusions in steels are not sufficiently small either to cause precipitation hardening or to prevent the movement of grain boundaries. Furthermore, their volume fraction is sufficiently low not to cause significant changes in strength as observed in composite reinforcement.

The understanding of these phenomena was limited for a long time by our ability to properly characterize materials. Ageing was a generic name for changes of properties with time that were first observed at room temperature and were quite puzzling. The hardening of aluminum alloy was taken advantage of well before it was properly understood and characterized [7,8]. The various facets of “ageing” of steel were also the reason for a wide range of speculations for some time [59]. Currently the usage of the term aging is more limited: in steel, mostly to strain aging while other

phenomena will be better referred to as precipitation hardening, as in the case of aluminum alloys. However, during heat treatment, the precipitation step after solubilization is still known as ageing.

4.1 Interactions with grain boundaries

Thorium oxide additions have been used to control grain growth in tungsten as rationalized and explained by Jeffries [60] in 1919, before the formulation of models for grain boundary pinning by particles.

Zener was the first to formulate a model in which small particles may limit the movement of grain boundaries [61,62]. While there is considerable discussion on the values of the coefficients to be used in Zener's equation, the behavior predicted by this equation is followed by various metals, including steel. Grain size is limited to a maximum value directly depending on the size of the particles and inversely related to the volume fraction of particles, as indicated in Figure 10. Detailed discussion of Zener's equation can be found in Refs [62-65]. This mechanism makes it possible to control the grain size of steels with relatively small volume fractions of very small particles. Typical examples for steels included in Figure 10 are AlN in austenite (commonly used in heat treatable steels) [24,66], MnS in austenite (relevant in electrical steels) [67-69], Nb(CN) in austenite (widely used in microalloyed HSLA steels and others) [70]. The wide range of particle-matrix combinations in Figure 10 shows how general the Zener behavior is. Gladman et al. have demonstrated that dispersed alumina, either introduced as particles in mechanical alloying or created in-situ by oxidation may also control austenitic grain growth [23] provided it is

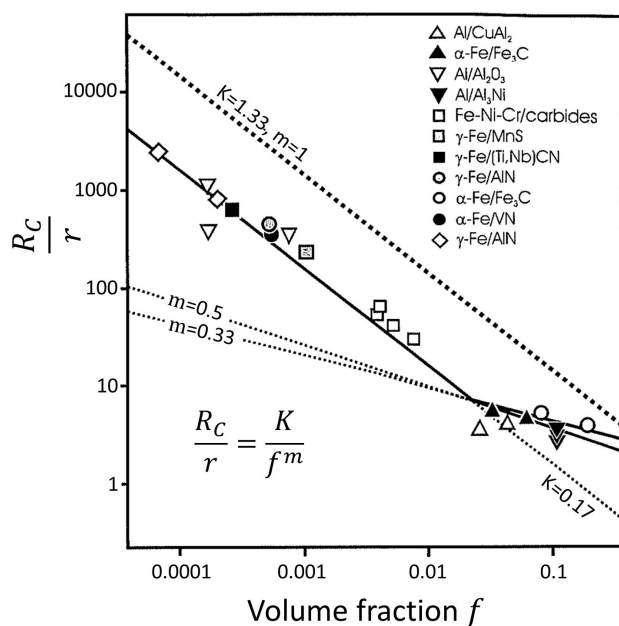


Figure 10. Relationship between maximum grain size in a material containing a dispersion of particles of radii r and volume fraction f . Various coefficients adjusted to the Zener-type equation. Data compiled by Manohar and co-workers. Adapted from [62].

sufficiently small. They also observed that larger particles formed from the melt are normally only able to control larger grain sizes in the HAZ of welds, but still in accordance with Zener type behavior [71,72].

Certain particles, with the right size and volume fraction can enhance the nucleation of acicular ferrite as recently reviewed by Loder et al. [73]. This was initially observed in weld metal (see Figure 2) [74]. These effects have been ascribed both to epitaxy [75] or to matrix depletion of austenite stabilizers [76,77]. In any case, size and distribution are essential variables to define the extent of the change in the microstructure of the metal [74]. Inoue and Koseki demonstrated the effectiveness of inoculation of steels with Ti and N to form particles in-situ and nucleate equiaxial ferrite grains from the liquid [78]. A recent project of the EU addressed the issue of adding particles and particle precursors to liquid steel, aiming at grain size control [79]. Various additions were tested, and the results were analyzed using pinning and nucleation models.

Figure 11 presents the recrystallization in a HSLA during controlled rolling compared to the calculated Zener factor $\left(\frac{f}{r}\right)$ for the precipitated carbonitride. The effect of the particles in preventing recrystallization is also well expressed by the Zener factor.

Small particles may also interact with dislocations resulting in precipitation hardening [82,83]. Mott and Nabarro were the first to formulate a model for this interaction in 1940. Ardell has reviewed the evolution of the theory of precipitation hardening [84]. Albeit interface coherence and precipitate ordering are important, the critical variables are size and spacing of particles, related through volume fraction. Equation 1 is a simple expression frequently used for the particle spacing (L) for uniformly distributed spherical particles of radius r and volume fraction f .

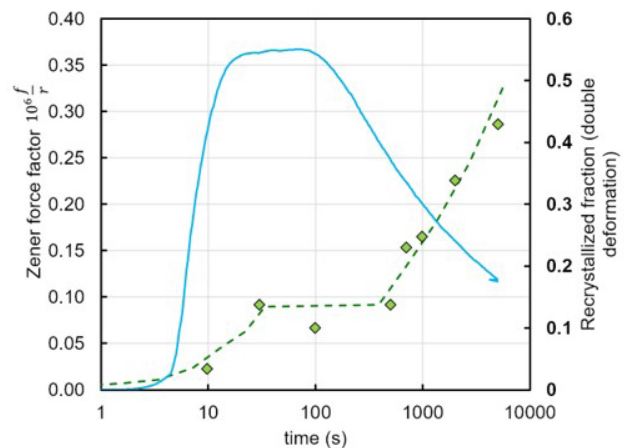


Figure 11. Zener force factor calculated using Vervynck's data in PRISMA, TCFE12 and MOBFE7 [80], and recrystallized fraction measured in double deformation tests for the same steel. Data from Vervynck et al. [81].

$$L = 4r/3f \quad (1)$$

The Ashby-Orowan equation [83,84] is a reasonable initial approximation for many cases. Equation 2 [85] presents the increase in shear stress ($\Delta\tau$) needed to move dislocations with a Burgers vector b through a dispersion of particles with uniform spacing L , in a material with a shear modulus G .

$$\Delta\tau = \frac{Gb}{L} \quad (2)$$

Figure 12 presents a comparison of strengthening effects as a function of volume fraction of carbonitride precipitates compared with experimental results in HSLA steels. It is important to observe the range of particle sizes that can cause precipitation hardening.

The analysis of microalloyed HSLA steels is further complicated that microalloying carbonitrides can and do precipitate, in some cases, before or during solidification either due to high additions of the solutes or to segregation. (e.g [80,87]). Thus, in the same steel one may have “larger” second-phase carbonitrides (such as “TiN” inclusions that will influence ductility and fatigue, for instance) as well as “smaller” second-phase particles ((Ti,Nb)(C,N); (Nb,Ti

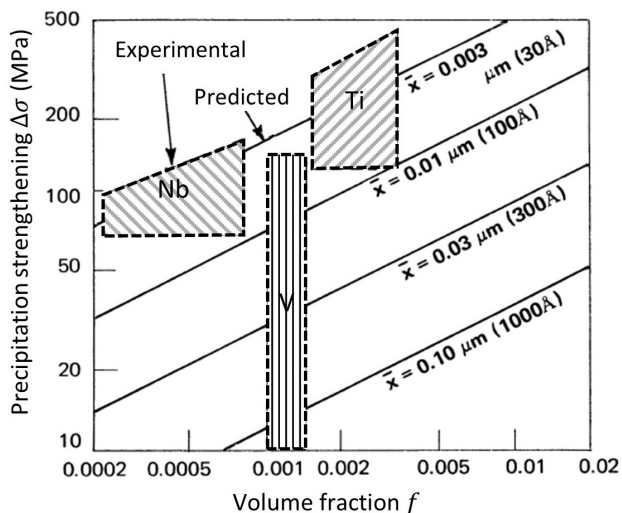


Figure 12. Precipitation hardening effect calculated according to the Ashby-Orowan equation for different particle sizes compared with experimental observations. Adapted from [86].

(C,N) as well as V(C,N)). High temperature solid state precipitation of Ti richer compounds may help control austenite grain growth, Nb rich carbonitrides as well as solute Nb will help control austenite recrystallization and austenitic grain growth, while typically V compounds (and perhaps interphase precipitated Nb compounds) will cause precipitation hardening. Furthermore, steel design may also take advantage of precipitation hardening by TiC and (Ti,Mo)C at lower temperatures [88-90].

Evidently, even if size and volume fraction control their effects on the steel, the chemical composition of the particles is essential to understanding the thermodynamics and kinetics of their formation and hence for steel design. This is valid not only for “precipitation” hardening and grain size control but also in inclusion engineering (e.g. Refs [3,76]).

5 Summary

The steel industry adopted the expression “second phase particles” many years ago. The expression became somewhat “all-encompassing”: this led to some significant difficulties in understanding the behavior of phases or “particles” dispersed in a steel matrix that may, itself, be multiphase. While non-metallic inclusions and many “precipitates” are cited as second phases their behavior can be significantly different in steel. In this review, we propose that size and volume fraction are the key characteristics to understand the behavior of a second phase in steel. Chemical composition, although of paramount importance in steel design and processing control is, alone, a poor guide to understanding their effect in steels except, perhaps in areas such as corrosion behavior. In structural applications, larger particles will affect mostly ductile fracture processes and fatigue while smaller particles will be effective in interfering with grain boundaries and dislocations. The type and strength of the particle-matrix interface would be an additional relevant criterion to consider. The critical size separating larger and smaller particles is somewhat dependent on the steel properties but in general, constituents in the micrometer range will be considered “larger” whereas nanometer sized particles will be able to interfere with dislocations and grain boundaries.

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