

# **Enabling Factors Toward Production of Nanostructured Steel On an Industrial Scale**

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## **Abstract**

Utilizing the existing properties of steel, a modern technological society has been constructed. While there are over 25,000 worldwide equivalent steels developed based on manipulating the eutectoid transformation, there are only a handful of existing commercial nanostructured steel alloys based on manipulating the more complex glass devitrification transformation. Thus, research on nanostructured steels is in its infancy and many further developments are expected with the demonstrated promise of developing new combinations of superior properties. In this paper, seven enabling metallurgical factors will be presented which will ultimately allow a variety of nanostructured steel products to be produced in an ever increasing array of industrial processing techniques. Additionally, a case example of the formation of nanostructured steel will be given showing how these factors can be harnessed on an industrial scale.

## **Introduction**

Steel has been used by mankind for at least 3,000 years and its pre-eminent position in modern society is a result of several favorable criteria including the abundance and low cost of iron, its main constituent, its manufacturing ability, and its recyclability. It has been very extensively studied over the centuries and more is known about steel than any other material. Steel in its various forms is widely utilized and comprises over 80% by weight of all metallic alloys in industrial use and is currently available in over 25,000 worldwide equivalents in 51 different ferrous alloy metal groups (1).

After several millennia and such extensive research, one may think that future developments in steel are part of the past and its full range of properties have been developed and exploited. As we enter the 21<sup>st</sup> century, advanced research in materials is expected to be focused on exotic “high tech” materials and the importance of steels are expected to diminish as newer and better materials are developed. But, could the future of steel follow a different path, perhaps one in which advanced research on steels, specifically nanostructured steels, flourishes? Additionally, will the near term future of nanomaterials technology be programmable assemblies, replicators, and swarms of nanomachines acting in unison as some have suggested, or perhaps instead the bulldozer, the mining crusher,

and the automobile? In this article, the author will present a vision of the future of nanostructured steel and will attempt to answer these questions via a critical analysis, broken down into seven key enabling metallurgical factors, which are expected to allow the development of nanostructured steel on an industrial scale.

### **1) The Very Nature of Steel**

Often when one thinks of steels, they are considered to be iron and carbon alloys. This definition is not incorrect but it applies generally to mild or plain carbon steels. A more appropriate textbook definition for steel would be; “Any iron based alloy in which no other single element is present in excess of 30 weight percent and for which the iron content amounts to, at least, 55 weight percent and carbon is limited to a maximum of 2 weight percent.” By utilization this definition of steel, one can quickly see the great potential for this class of materials. One of the hottest research areas over the last two decades has been in the area of high energy density rare earth permanent magnets specifically based on the high magnetocrystalline anisotropy of the  $\text{Nd}_2\text{Fe}_{14}\text{B}_1$  phase. The  $\text{Nd}_2\text{Fe}_{14}\text{B}_1$  phase, which contains 72 wt% Fe, 27 wt% Nd, and 1 wt% B, has a composition that clearly fits the definition of steel. Thus, from this respect, steels have already been on the cutting edge of research in the permanent magnet community and this prominence in research may only be expected to grow.

### **2) The Strength / Properties of Existing Steels**

During the 1920's, physicists first began to calculate the strength of the atomic bonds and it was discovered that the measured experimental strength of materials was far lower than their theoretical strength, independent of the primary nature of the bonds (i.e. metallic, covalent, or ionic). Based on the metallic bonding in iron, the theoretical tensile strength has been calculated to be 13.2 GPa (2) but high strength steels, even today, only typically achieve maximum tensile strength levels up to 1.5 GPa. Thus, our modern technological society has been established utilizing the 5 to 10% strength level of iron. This realization opens up a very large area of potential improvement if the existing strength of the iron metallic bond could be effectively harnessed.

In the 1960's, several groups of scientists began working on developing near defect free materials called “whiskers”. The whiskers were very small filaments which were precipitated from liquid solution or by vapor phase condensation and were of appropriate form that they could be used for specialized tensile testing. In the best cases, whiskers were produced that were essentially defect free and the highest measured tensile properties measured for iron were 12.6 GPa (2), which represents 95% of theoretical. Thus, studies on near perfect whiskers validated both the approach toward strengthening and the theoretical calculations while additionally setting a benchmark for future achievement. However, attempts at trying to consolidate the whisker materials into bulk shapes while maintaining their unique properties were unsuccessful since thermodynamically stable defects formed during the consolidation process. Thus, while it has been shown that the *paradox* can be exceeded, for four decades, it has not been clear how to successfully do this on an industrial scale.

### 3) Solid State Transformation For Microstructural Development

The development of steel microstructures is based on the manipulation of a very specific solid/solid state transformation called a eutectoid transformation (i.e.  $\gamma_{\text{austenite}} \Rightarrow \alpha_{\text{ferrite}} + \text{Fe}_3\text{C}_{\text{cementite}}$ ). To achieve a targeted set of properties, the austenite ( $\gamma$ ) precursor, which represents a supersaturated solid solution, can be transformed into combinations of ferrite ( $\alpha$ ) and cementite ( $\text{Fe}_3\text{C}$ ) phases in a wide variety of distinct microconstituent microstructures containing pearlite, upper bainite, and lower bainite. Alternatively, the austenite can be transformed through a diffusionless shear transformation into a body centered tetragonal martensitic structure. Thus, the control of the eutectoid transformation is the primary factor resulting in the wide variety of existing structures and resulting properties found in commercial steel alloys.

To develop nanostructured steels, there is another analogous solid state transformation that can be employed called glass devitrification. In this case, the supersaturated solid solution precursor material is a supercooled liquid, called a metallic glass. The key is that the glass structure eliminates entire classes of defects including 1-d dislocations and 2-d grain and phase boundaries. Unfortunately, the glass is not a defect free material, since it contains a large fraction of free volume defects so the full strength of the iron atomic bond is not realized. Upon subsequent heating, the metallic glass precursor transforms into multiple solid phases through devitrification. In glass forming steel systems, depending on the specific composition, the crystallization temperatures usually is in the range from 500°C to 650°C and the enthalpy of the glass to crystalline transformation varies from -75 J/g to -200 J/g. Since the glass forming steels commonly melt at 1100 to 1250°C, this means that the glass devitrification occurs at low fractions of the melting temperature ( $\approx 0.5 T_m$ ) where diffusion is limited and where the driving force, due to the metastable nature of the glass state, is extremely high. Thus, during devitrification a very high nucleation frequency occurs with limited time for grain growth before impingement between neighboring grains. Analogous to the characteristic microstructures developed from the eutectoid transformation, the devitrified steels form specific characteristic microstructures which are nanoscale.

### 4) The Enabling Complexity of the Glass Devitrification

Quenching austenite to form metastable martensite has been enabling in the development of conventional steels. Analogously, there are several enabling advantages of the devitrification transformation. In conventional processing, the solubilities of alloying elements are limited but due to the nonequilibrium nature and liquid like structure of the glass, solid solubilities can be dramatically widened and atoms which are normally not compatible can be brought into close contact. For example, consider the neodymium iron binary phase diagram which shows that neodymium has a maximum solubility in austenite at elevated temperature of 4.0 wt% and no solubility at room temperature. In a steel glass, it is possible to dissolve up to 30 wt% neodymium in the glass and maintain this solubility at room temperature.

Additionally, the glass devitrification transformation is found to be incredibly complex and even when the composition is fixed, even more variability is obtained by varying the transformation pathway of the glass devitrification transformation. The thermal history of the transformation is important and glass relaxation, recovery, crystallization, and recrystallization phenomena are all important factors resulting in microstructural development (3). By manipulating these effects, the microstructure can be engineered in a variety of fashions including varying the average phase size, causing precipitation in the glass or in the nanocomposite and even forming anisotropic or isotropic microstructures (for example see Figure 1).

### **5) Overcoming The Weak Link in Steel Processing**

In conventional steels, solidification is the weak link since during the stochastic solidification process, alloying elements redistribute and segregate as a result of the complex series of solidification events which can occur under nonequilibrium conditions. In binary systems, the three phase reactions are well understood but the complexity of these invariant reactions increases dramatically as the number of components (i.e. elements) is increased. The degrees of freedom available to the system can be described by the Gibbs Phase Rule and even if pressure is held constant one finds quickly the enormous complexity of understanding solidification in multicomponent systems.

However, in glass forming alloys, it is possible to effectively study alloys containing large number of elements (i.e. 7 to 11+ elements) since all microsegregation can be avoided by solidifying directly into a glass structure (4). This uniform starting condition is easy to describe metallurgically and if transformed, with a one stage heat treatment significantly above the glass crystallization temperature, relaxation, recovery, and recrystallization phenomena can be avoided. Consider an eight element glass forming steel composition containing iron, chromium, molybdenum, tungsten, boron, carbon, silicon, and manganese. Fully understanding the complex solidification sequence leading to the cast ingot structure shown in Figures 2a and 2b, would require an effort somewhat analogous to the moon launch. However, the microstructure of the as-solidified glass Figure 2c is easily described even though the darkfield micrograph shows the presence of embryos (i.e. crystalline nuclei). After heat treating above the crystallization temperature, a uniform microstructure is formed consisting of a three phase matrix with 'clean' grain boundaries which represents a structure which is much less complex than the crystalline cast ingot structure (Figure 2d). Thus, while conventional steels have been developed using relatively small numbers of alloying elements due to the complexity of understanding solidification and controlling structure, by avoiding solidification and forming a glass, the complexity is significantly reduced and large numbers of atoms can be effectively alloyed to achieve specific property goals.

## **6) Demonstrated Advances in Mechanical Properties**

Analysis of the *strength of materials paradox*, shows the potential of developing much higher strengths in steel alloys and the paradox can indeed be exceeded through the glass devitrification route. In nanostructured steel alloys, we have measured tensile strengths over 4 GPa at 20°C and strength levels of 1.8 GPa at 750°C, which is stronger than conventional steels at room temperature. However, the real promise of this approach is to separate out the physical mechanisms governing strength and hardness with those governing toughness and ductility and then subsequently and independently optimize both to overcome the existing inverse relationship between strength and toughness found in conventional materials. Towards this end, we have recently shown that superplasticity can be obtained with a very high tensile elongation of 230% in a nanocomposite steel alloy produced from metallic glass precursors (5). The measured strain rate sensitivity factor of 0.51 shows that the primary mechanism controlling deformation was not dislocation motion but grain boundary sliding and rotational processes, which were enabled by the extremely fine nanoscale grain size. The ability to shrink the scale of the microstructure to the nanoscale will enable new mechanisms to control mechanical properties allowing new combinations of properties, such as strength and toughness, which are not possible on conventional length scales.

## **7) Ability to Form Bulk Steel Glasses**

Since a steel metallic glass precursor must be produced, one may assume that rapid solidification is necessary and that the realm of nanostructured steels will never be possible with conventional metallurgical processes such as casting. However, this belief is not correct since there has been a recent explosion in metallic glass research showing that bulk glass formation is possible in a wide variety of base material systems including zirconium (6-8) nickel (9), magnesium, rare earths (10,11), and iron (12-14). In the best cases glass formation can occur down to the 1 K/s (7) cooling range. While the glass state has interesting properties including high elasticity and low friction, perhaps the biggest factor is to devitrify the glass into a nanocomposite structure. The challenge is not just to form a bulk glass but one that can be devitrified into a nanocomposite structure which has favorable combinations of properties. Thus, with the demonstration of bulk glass now firmly established, it appears only a matter of time before bulk glass forming steels will be developed on an industrial scale.

## **Industrial Example Of Nanostructured Steel**

As a case example of using the 7 enabling factors to develop industrial products, consider high performance coatings. Conventional approaches toward forming nanoscale coatings have relied on producing nanoscale particulates or heavily mechanically worked powders and then trying to maintain the nanoscale structure during heat up in the spray and subsequent impingement (15-17). An alternate approach is to use conventionally sized powder for HVOF, or conventionally sized cored wire for wire arc, and then produce nanoscale coatings by devitrifying directly from an amorphous precursor (18). As an example of this approach, consider the devitrified TEM microstructures of our commercial steel SHS717 alloy shown for the “ideal” targeted microstructure, the HVOF coating, and

the wire-arc coating in Figures 3a, 3b, and 3c respectively. While the coating structures are coarser than the 'ideal' structure and additionally contain isolated larger scaled regions which formed during solidification, they are still nanoscale which is remarkable considering that they were processed in air using off the shelf thermal spray technology.

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## Figures

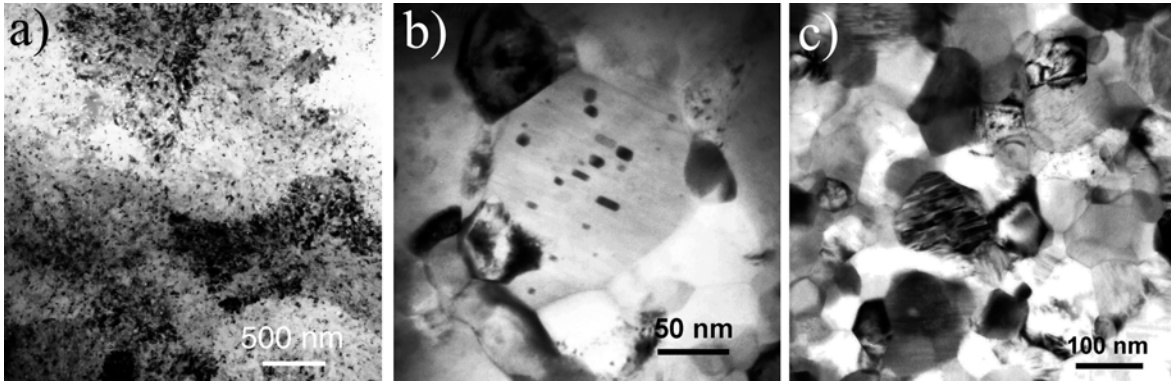


Figure 1 Example TEM micrographs showing the changes in structure possible by varying the crystallization conditions of an amorphous steel. a) 500°C for 100 hour heat treatment showing anisotropic microstructure with 1 to 2 micron aligned regions containing 20 nm cellular grains, b) 300°C for 100 hour, 700°C for 10 minute two step heat treatment showing  $\alpha$ -Fe nanoprecipitates which originally formed in the glass and then were contained in the crystalline phases after complete crystallization, c) 700°C for 10 minute heat treatment showing a 3 phase matrix structure with no precipitates.

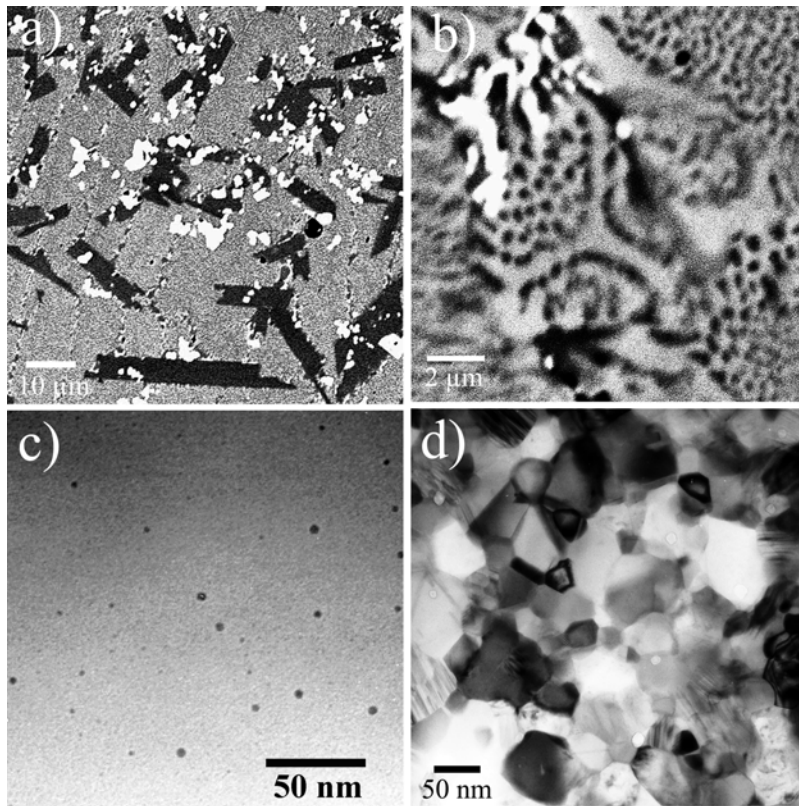


Figure 2 Electron micrographs of a specific eight element glass forming steel composition which has been either cast or rapidly solidified. a) SEM micrograph of cast structure (low mag), b) SEM micrograph of cast structure (high mag), c) Darkfield TEM micrograph of the rapidly solidified steel structure showing the glass structure containing embryos, d) TEM micrograph of the rapidly solidified steel which has been heat treated at 700°C for 10 minutes.

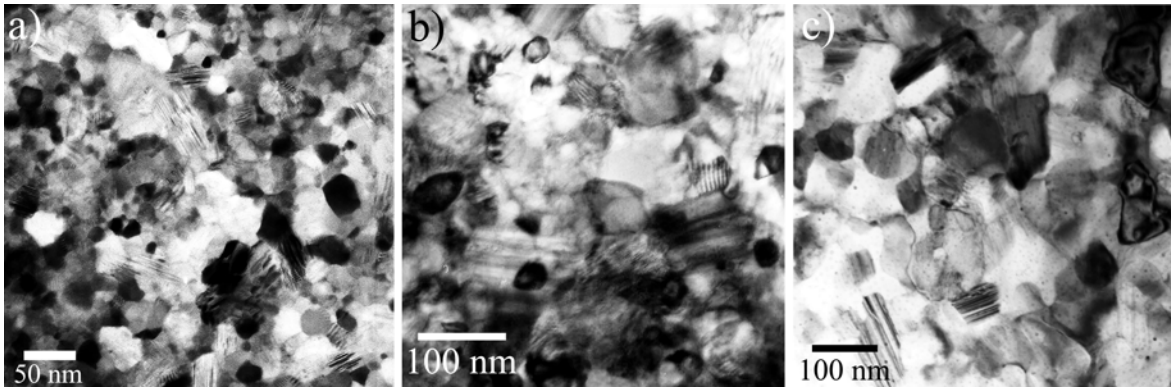


Figure 3 TEM micrographs of an eight element glass forming steel alloy (SHS717) which has been devitrified at 700°C for 10 minutes. a) Melt-spun ribbon (average grain size 25 nm), b) HVOF coating (average grain size 50 nm), c) wire-arc coating (average grain size 80 nm).