Enabling Factors Toward Production of Nanostructured Steel on an Industrial Scale

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Utilizing the existing properties of steel, a modern technological society has been constructed. While there are over 25,000 worldwide equivalent steels based on manipulating the eutectoid transformation, there exist only a handful of 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 article, seven enabling metallurgical factors are presented that 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 are given showing how these factors can be harnessed on an industrial scale.

1. Introduction

Steel has been used by mankind for at least 3000 years, and its preeminent position in modern society is a result of several favorable criteria, including the abundance and low cost of iron, its manufacturing ability, and its recyclability. Steel has been very extensively studied over the centuries, and more is known about it than about any other material. Steel in its various forms is widely used, comprises over 80 wt.% of all metallic alloys in industrial use and is currently available in over 25,000 worldwide equivalents in 51 different ferrous alloy metal groups (Ref 1).

After several millennia and extensive research, one may think that future developments in steel are part of the past, and that its full range of properties has been developed and exploited. As society enters the 21st century, advanced research in materials is expected to focus on exotic "high-tech" materials, and the importance of steels is expected to diminish as newer and better materials are developed. However, 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 nanomaterial technology be in programmable assemblies, replicators, and swarms of nanomachines acting in unison, as some have suggested, or perhaps instead in the bulldozer, the mining crusher, or the automobile? In this article, a vision of the future of nanostructured steel is presented, and an attempt to answer these questions via a critical analysis of seven key enabling metallurgical factors is made.

2. 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 wt.%, and for which the iron content amounts to at least 55 wt.% and carbon is limited to a maximum of 2 wt.%. By utilizing 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 those based on the high magnetocrystalline anisotropy of the $Nd_2Fe_{14}B_1$ phase. The $Nd_2Fe_{14}B_1$ phase, which contains 72 wt.% Fe, 27 wt.% Nd, and 1 wt.% B, has a composition that clearly fits the definition of steel. Thus, steels have already been on the cutting edge of research in the community of investigators researching permanent magnet, and this prominence in research may only be expected to grow.

3. The Strength/Properties of Existing Steels

During the 1920s, 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 (Ref 2), but high-strength steels, even today, typically achieve maximum tensile strength levels up to 1.5 GPa. Thus, modern technological society has been established utilizing only 5 to 10% of the strength level of Fe. This realization opens up a very large area of potential improvement if the existing strength of the Fe metallic bond can be effectively harnessed.

In the 1960s, several groups of scientists began working on developing near-defect-free materials called "whiskers." The whiskers were very small filaments that 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 tensile properties

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measured for Fe were 12.6 GPa (Ref 2), which represents 95% of theoretical predictions. Thus, studies on near-perfect whiskers validated both an approach toward strengthening and the theoretical calculations for strength, 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 because 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.

4. Solid-State Transformation for Microstructural Development

The development of steel microstructures is based on the manipulation of a very specific solid-state/solid-state transformation called a eutectoid transformation (i.e., $\gamma_{austenite} \rightarrow \alpha_{ferrite} + Fe_3C_{cementite}$). To achieve a targeted set of properties, the austenite (γ) precursor, which represents a supersaturated solid solution, can be transformed into combinations of ferrite (α) and cementite (Fe_3C) 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 used 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 one-dimensional dislocations, and two-dimensional grain and phase boundaries. Unfortunately, the glass is not a defect-free material, because it con-

tains a large fraction of free volume defects so that the full strength of the Fe atomic bond is again not fully 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 temperature is usually in the range from 500 to 650 °C, with the enthalpy of the glass-to-crystalline transformation varying from −75 to −200 J/g. Because the glass-forming steels commonly melt at 1100 to 1250 °C, this means that the glass devitrification occurs at a low fraction of the melting temperature (~0.5 T_m) where diffusion is limited and 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 that are nanoscale.

5. 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 that are normally not compatible can be brought into close contact. For example, consider the Nd-Fe binary phase diagram, which shows that Nd has a maximum solubility in austenite at an 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.% Nd in the glass and maintain this solubility at room temperature.
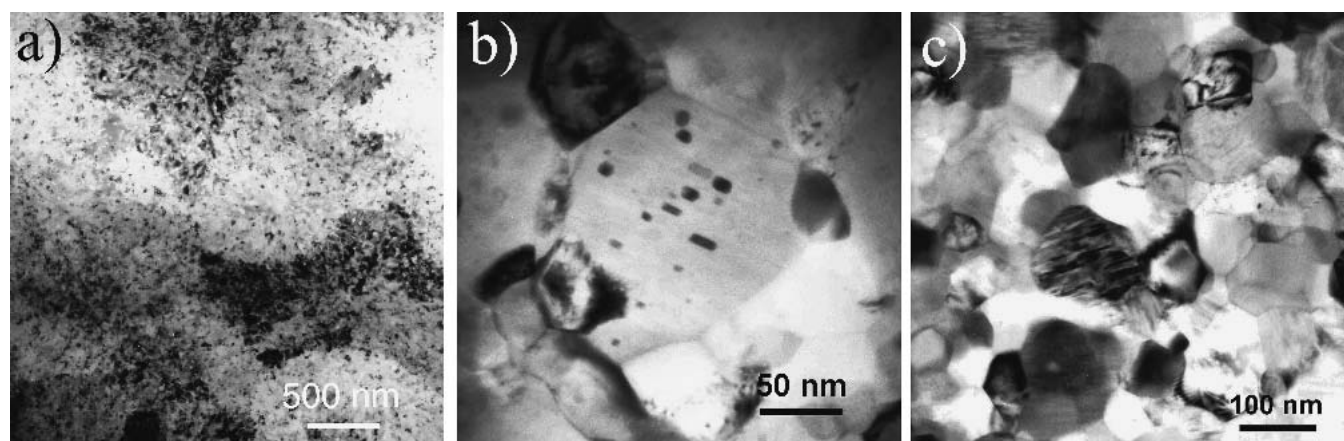

Fig. 1 TEM micrographs showing the changes in structure that are possible by varying the crystallization conditions of an amorphous steel. (a) Heat treatment at 500 °C for 100 h showing anisotropic microstructure with 1 to 2 μm aligned regions containing 20 nm cellular grains. (b) Two-step heat treatment at 300 °C for 100 h and 700 °C for 10 min, showing αFe nanoprecipitates that originally formed in the glass and then were contained in the crystalline phases after complete crystallization. (c) Heat treatment at 700 °C for 10 min showing a three-phase matrix structure with no precipitates

Additionally, the glass devitrification transformation has been found to be incredibly complex, and, even when the composition is fixed, more variability is obtained by altering 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 (Ref 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 (e.g., Fig. 1).

6. Overcoming the Weak Link in Steel Processing

In conventional steels, solidification is the weak link during the stochastic solidification process, because alloying elements redistribute and segregate as a result of the complex series of solidification events that can occur under nonequilibrium con-
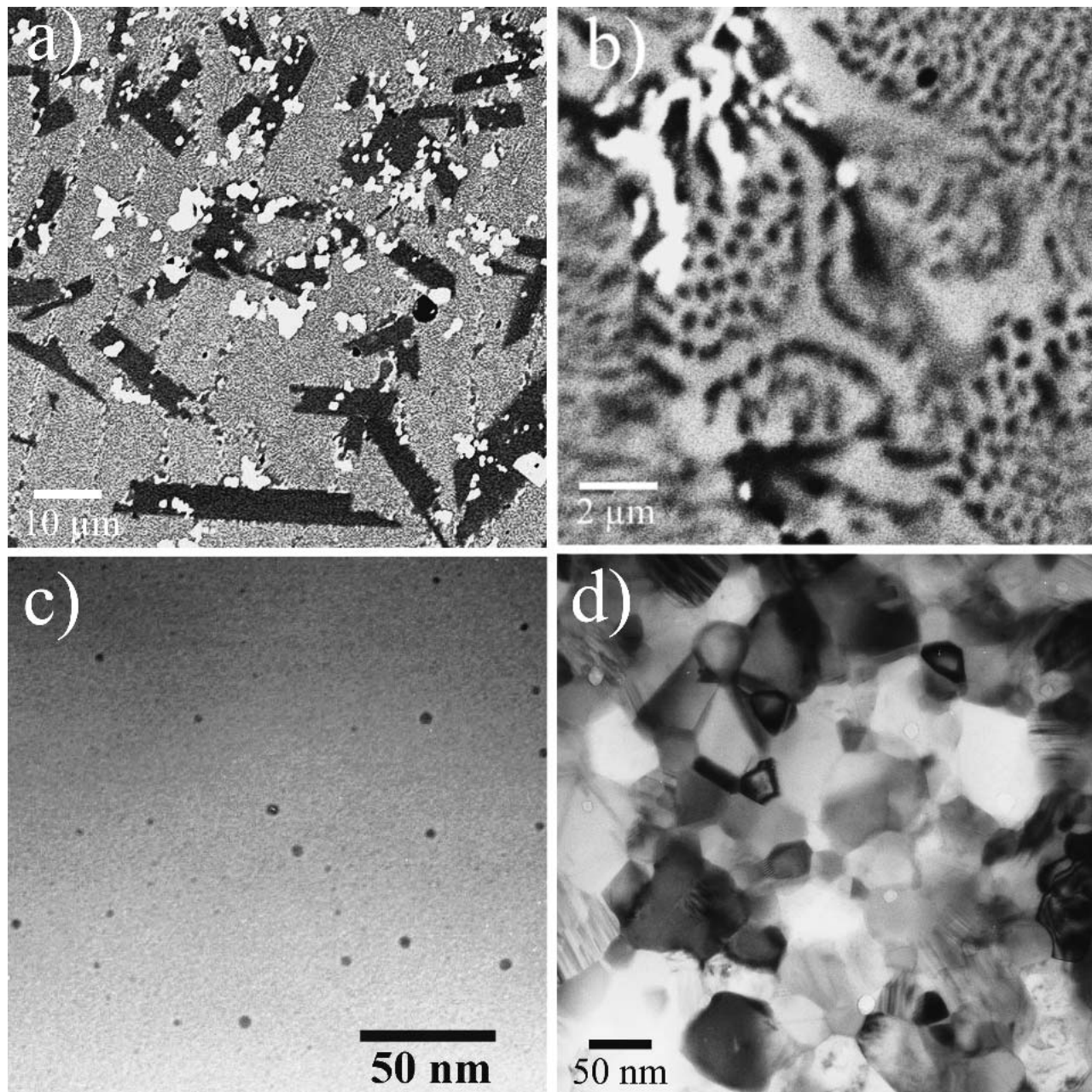

Fig. 2 Electron micrographs of a specific eight-element glass-forming steel composition that has been either cast or rapidly solidified. (a) SEM micrograph of cast structure (low magnification). (b) SEM micrograph of cast structure (high magnification). (c) Dark-field TEM micrograph of the rapidly solidified steel structure showing the glass structure containing embryos. (d) TEM micrograph of the rapidly solidified steel that has been heat treated at 700 °C for 10 min

ditions. 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 that are available to the system can be described by the Gibbs phase rule, and, even if pressure is held constant, one understands quickly the enormous complexity of understanding solidification in multicomponent systems.

However, in glass-forming alloys, it is possible to effectively study alloys containing a large number of elements (i.e., 7–11+ elements) because all microsegregation can be avoided by solidifying directly into a glass structure (Ref 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 containing Fe, Cr, Mo, W, B, C, Si, and Mn. Fully understanding the complex solidification sequence leading to the cast ingot structure shown in Fig. 2(a) and (b) would require an effort somewhat analogous to the moon launch. However, the microstructure of the as-solidified glass seen in Fig. 2(c) is easily described, even though the dark-field 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 that is much less complex than the crystalline cast ingot (Fig. 2d). Thus, while conventional steels have been developed, using relatively small numbers of alloying elements due to the complexity of understanding solidification and controlling the microstructure, 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.

7. Demonstrated Advances in Mechanical Properties

An analysis of the strength of the materials paradox shows the potential of developing much higher strengths in steel al-loys, and the paradox can indeed be exceeded through the glass devitrification route. In nanostructured steel alloys, measured tensile strengths have exceeded 4 GPa at 20 °C, and strength levels of 1.8 GPa at 750 °C have been obtained, which is stronger than conventional steels at room temperature. However, the real promise of this approach is to differentiate 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. Toward this end, it has recently been shown that superplasticity can be obtained with a very high tensile elongation of (i.e., >230%) in a nanocomposite steel alloy produced from metallic glass precursors (Ref 5). The measured strain rate sensitivity is 0.51, which shows that the primary mechanism controlling deformation is not dislocation motion, but rather grain boundary sliding and rotational processes, which are enabled by the extremely fine nanoscale grain size. The ability to shrink the scale of the microstructure to the nanoscale will enable new mechanisms for controlling mechanical properties and will allow new combinations of properties, such as strength and toughness, which are not possible with conventional length-scale microstructures.

8. Ability to Form Bulk Steel Glasses

Because 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 because 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 Zr (Ref 6-8), Ni (Ref 9), Mg, rare earth elements (Ref 10, 11), and Fe (Ref 12-14). In the best cases, glass formation can occur for cooling rates approaching 1 K/s (Ref 7). While the glass state has interesting properties, including high elasticity and low friction, perhaps the most important factor is the possibility of devitrifying the glass
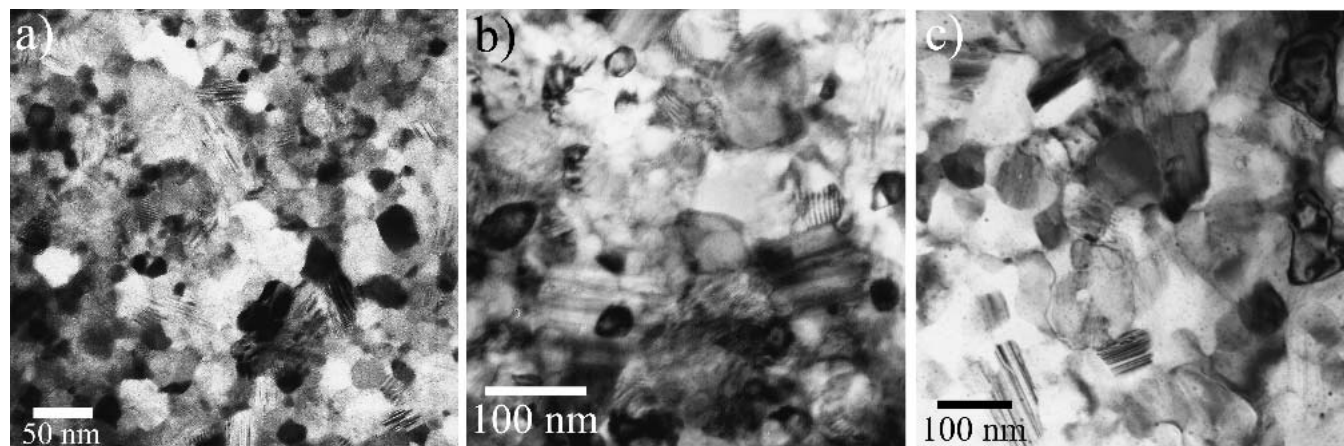

Fig. 3 TEM micrographs of an eight-element glass-forming steel alloy (SHS7170), which has been devitrified at 700 °C for 10 min. (a) Melt-spun ribbon (average grain size 25 nm). (b) HVOF coating (average grain size 50 nm). (c) Wire-arc coating (average grain size 80 nm)

into a nanocomposite structure. The challenge is not just to form a bulk glass but a glass that can be devitrified into a nanocomposite structure that has favorable combinations of properties. Thus, with the demonstration of bulk metallic glass now firmly established, it appears only a matter of time before bulk glass-forming steels will be developed on an industrial scale.

8.1 Industrial Example of Nanostructured Steel

As a case example of using the seven 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 (Ref 15-17). An alternate approach is to use conventionally sized powder for high-velocity oxyfuel (HVOF), or conventionally sized cored wire for wire arc, and then to produce nanoscale coatings by devitrifying directly from an amorphous precursor (Ref 18). As an example of this approach, consider the devitrified transmission electron microscopy (TEM) microstructures of a commercial SHS7170 alloy, which is shown for the "ideal" targeted microstructure, the HVOF coating, and the wire-arc coating in Fig. 3(a) to (c), 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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