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Review

Heuristic Design of Advanced Martensitic Steels That Are Highly Resistant to Hydrogen Embrittlement by ε-Carbide

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Abstract: Many advanced steels are based on tempered martensitic microstructures. Their mechanical strength is characterized by fine sub-grain structures with a high density of free dislocations and metallic carbides and/or nitrides. However, the strength for practical use has been limited mostly to below 1400 MPa, owing to delayed fractures that are caused by hydrogen. A literature survey suggests that ε-carbide in the tempered martensite is effective for strengthening. A preliminary experimental survey of the hydrogen absorption and hydrogen embrittlement of a tempered martensitic steel with ε-carbide precipitates suggested that the proper use of carbides in steels can promote a high resistance to hydrogen embrittlement. Based on the surveys, martensitic steels that are highly resistant to hydrogen embrittlement and that have high strength and toughness are proposed. The heuristic design of the steels includes alloying elements necessary to stabilize the ε-carbide and procedures to introduce inoculants for the controlled nucleation of ε-carbide.

Keywords: steel; martensitic steel; ε-carbide; tempering; hydrogen embrittlement; mechanical strength; inoculant; materials design

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1. Introduction

High-strength low-carbon martensitic steels yield low-cost environmentally efficient materials. Wider use of these materials could improve energy savings and reduce the carbon footprint of many products. The use of such steels in martensitic condition provides a good weldability and a high strength, which makes them attractive materials for structural applications. However, an increase in steel strength enhances hydrogen embrittlement (HE). For example, the strength of steel bolts for automobiles has been limited to 1400 MPa because of HE. In hydrogen-powered vehicles, steel with a high resistance to HE is required for cost and weight reductions [1]. A promising approach to develop steels with a high strength and a low HE susceptibility may be through the use of ε-carbide precipitates in steels. In this work, a conceptual design of advanced steels with a high resistance to HE is proposed based on a literature survey and on experimental results of the influence of ε-carbide on the HE susceptibility of steel.

The paper is organized as follows. Section 2 presents a critical literature review on hydrogen absorption of ε-carbide and steel precipitation strengthening. Section 3 presents preliminary experimental results on the influence of ε-carbide in martensitic steel on the HE susceptibility. In Section 4, a steel design with a high strength that is compatible with a low HE susceptibility is proposed. The design includes alloying elements that are required to stabilize ε-carbide and inoculants to nucleate ε-carbide precipitates. The final section provides concluding remarks.

2. Literature Survey

2.1. ε-Carbide and Hydrogen Embrittlement

Hughes et al. [2] first related the delayed fracture tests of a low-alloy steel in corrosive environments to ε-carbide precipitates in the steel microstructure. Their conjecture was based on Berg's paper [3], which indicated that ε-carbide would have a high affinity for hydrogen. This report is critically reviewed below.

Berg thought that ε-carbide in steel might hold and bind hydrogen. If so, the ε-carbide could reduce negative effects of hydrogen in steels, such as fish-scaling and embrittlement. At that time, it was assumed that ε-carbide was a hexagonal carbide transient to χ-carbide (Hägg carbide) with a composition of Fe_2C. In addition, the X-ray powder diffraction analysis ability was limited. He aimed to prepare the carbide starting from an iron catalyst following the method by Hofer et al. [4]. A mixture of oxides, Fe_2O_3 (142 gm), CuO (12.5 gm), and KOH (0.38 gm) was heated to 200 °C in a stream of H_2 of commercial purity for 1 week, and then heated to 170 °C in a stream of CO of commercial purity for 2 weeks. The CO gas contained 1% H_2 as an impurity gas. The mixture was enclosed in four porcelain tubes with perforated end disks and placed in a row in a quartz tube. The gases were forced to flow through the tubes. The first product of carburization in CO was supposed to be carbonyl hydride that was then converted into carbide. The contents of the four porcelain tubes were analyzed separately for C and H. The content of Fe was not analyzed. The chemical analysis yielded a close coincidence of the percentage of C and H on the atomic weight basis. This was the basis of Berg's conclusion that the carbide held hydrogen up to the composition of Fe_2HC. The hydrogen atoms incorporated into the carbide were thought to have originated from the impure CO gas.

Berg, however, did not identify the reaction product of X-ray structural analysis, nor was it identified by the temperature dependence of the magnetization. Therefore, it remains doubtful if his carbide was a single-phase Fe_2C. In fact, the iron carbide prepared by Hofer et al. with the same method was a magnetic mixture of hexagonal Fe_2C (60%) and χ-carbide (40%) [4]. Because the Curie temperature of the former is 380 °C and the latter 250 °C, Berg could have discriminated the two phases in his sample. Furthermore, his chemical reaction product could have contained iron carbonyl or metallic iron. More importantly, the hexagonal Fe_2C, which he had intended to prepare, was later confirmed to be monoclinic Fe_5C_2 by a precise X-ray analysis [5]. Today, the ε-carbides precipitated in steels are established as hexagonal $Fe_{2.4}C$ by the precise counting of Fe and C atoms in ε-carbide precipitates using atom-probe tomography [6,7].

In summary, Berg carried out an imperfect synthesis of a carbide that is different from the ε-carbide precipitated in steel. At best, he prepared a carbide, which is nowadays termed monoclinic Fe_5C_2. Accordingly, his conclusion that the carbide holds hydrogen up to Fe_2HC lacks experimental verification. No direct evidence has been presented for Fe_5C_2 precipitation by tempering of martensitic steels [8]. This literature survey indicates that Hughes's discussion [2] on HE of steel that relies on the Berg study has no sound foundations.

Recently, hydrogen trapping in a high-strength steel was reported by Zhu et al. [9]. Hydrogen was charged electrochemically at room temperature into a tempered martensitic steel with ε-carbide precipitates. The electrolyte was an aqueous solution of 0.5 M H_2SO_4, and the current density was 30 mA/cm^2. The influence of hydrogen charging on the tensile elongation was tested. The thermal desorption spectrum of the steel charged for 5 min revealed two peaks: a strong one at ~90 °C and a weak one at ~400 °C. The former was correlated to diffusive hydrogen (0.62 wppm) in the steel lattice and the latter to non-diffusive hydrogen trapped at the ε-carbide (0.31 wppm). It was concluded that the ε-carbide precipitates played a limited role in the alleviation of HE. They also measured concentration profiles of C and H across an ε-carbide precipitate with three-dimensional atom probe tomography. The values were ~11 at % for C and ~0.4 at % for H. This implies that the ε-carbide in their experiment may be formulated as $Fe_{2.4}CH_{0.04}$. It is not clear if this value represents the full hydrogen-trapping capacity of ε-carbide.

2.2. Precipitation Strengthening by ε-Carbide

Leslie was the first to note the possibility of precipitation strengthening of ferrite by ε-carbide, although he termed it as "metastable carbide" [10]. Leslie studied the aging of Fe–0.014% C, Fe–0.45% Mn–0.017% C, and Fe–3.25% Si–0.029% C alloys at 60–200 °C, after quenching from 730 °C. He noted two distinct configurations of the precipitated

carbides, long chains of carbide particles on dislocation lines and single particles in the matrix. The main changes in mechanical properties during the quench-aging resulted from the closely spaced carbides that precipitated within the matrix. He suggested Orowan's equation [11] as the underlying mechanism. The matrix nucleation sites for the ε-carbide remained undefined.

A search for the role of alloying elements on the nucleation of ε-carbide in Fe–C alloys has been reported for titanium, vanadium, and chromium [12]. Fine precipitates of TiC of 8~30 nm in size were found to act as preferential nucleation sites. The TiC particles formed during the alloy preparation and remained undissolved during subsequent solution treatment at 720 °C. The roles of V- and Cr-carbides remained unclear because of the limited additions of vanadium and chromium to the Fe–C alloys.

Isolated cases of the role of ε-carbide in engineering steels have been reported. Eglin steel is an ultra-high-strength steel alloy that was developed at Eglin Air Force Base in the early 2000s and was patented in 2009 [13]. The steel has strength levels like AerMet100, AF1410, and HP9–4–30 but is produced at a reduced cost because of the reduction or elimination of expensive alloying elements, such as nickel and cobalt. A comprehensive study followed to correlate the mechanical properties and microstructural evolution in the heat-affected zone of the Eglin steel [14]. ε-carbide particles were found in an auto-tempered lath of martensite in the coarse grains of the heat–affected zone (HAZ) of Eglin steel. The ε-carbide particles improved the HAZ toughness significantly.

Abrahams (author in [14]) invented a "low alloy high performance steel". The patent application was filed in 2016 and patented in the United States in 2019 [15]. The steel composition was 0.24%~0.32% C, 2.00%~3.00% Cr, 0.50%~1.50% Mo, 0.05%~0.35% V, 1.00% Mn or less, ~3.00% Ni or less, and ~1.50% Si or less, with a balance of Fe. The hardened and tempered article had a high impact toughness and other favorable physical properties such as an ultimate tensile strength, yield strength, elongation to failure, and hardness. The steel is believed to have been strengthened by nanoscale ε-carbides within a primarily martensitic matrix. The carbide was 100~150 nm long and ~10 nm wide. The carbide particles have a feathery rod-like shape, which are semi-coherent to the matrix. According to the inventor, without being bound by any theory, ε-carbide is believed to provide strength while preserving the dynamic toughness.

Xia et al. developed a low-carbon high-silicon martensitic steel in which ε-carbide plays a role [16]. The chemical composition is 0.21% C–1.8% Si–1.1% Mn–0.7% Cr–0.14% Ni–0.19% Mo. The steel has a tensile strength of 1548 MPa, an impact toughness of 120 J/cm^2, and a fracture toughness (K_{IC}) of 94.8 MPa m$^{1/2}$ when it is austenitized at 900 °C for 1 h followed by water quenching and then tempered at 320 °C for 1 h. Its microstructure is characterized by lath martensite, retained austenite films, and ε-carbide. The ε-carbides are present as short flakes in the martensite matrix and enhance the steel toughness.

At the end of Section 2.2, a comment is provided on low-temperature-tempered (LTT) martensitic steels, typically 4130 and 4340 steels. A review on this technology has been given by Krauss [17]. The low-temperature tempering of quenched martensite between 150 and 200 °C improves its toughness but maintains its hardness and strength at a high level. This increase in strength is attributed to the effect of increasing the density of fine-transition carbides, believed to be orthorhombic η-carbide, on the strain-hardening behavior of the martensitic microstructures. The chemical composition of the η-carbide was assumed to be between that of Fe_2C and Fe_3C. However, controversy existed between orthorhombic η-carbide and hexagonal ε-carbide. Thompson investigated this question using imaging and electron diffraction techniques with a transmission electron microscope [18] and found that the distinction between orthorhombic and hexagonal carbides appeared unlikely; η-carbide and ε-carbide that were observed by electron diffraction patterns were nearly the same. Therefore, fine transition carbides in LTT martensitic steels are ε-carbides. The HE susceptibility of LTT martensitic steels was outside of the research interest, whereas that of high-temperature-tempered LTT steels (tempered at ~600 °C) has been reported because of their application in oil and gas engineering in environments that contain H_2S [17].

3. Experiments on Hydrogen Absorption

The literature suggests that ε-carbide precipitation is a promising tool to increase steel strength and toughness if the size and dispersion are controlled. However, the influence of ε-carbide on HE has not been studied extensively. If ε-carbide increases the storage capacity of hydrogen of the steel, it will extend the time required to provide sufficient hydrogen atoms for the formation of hairline cracks.

To evaluate the HE susceptibility of steels, an easy and precise testing method has been proposed, namely immersion hydrogen charging with ammonium thiocyanate (NH_4SCN) solution [19]. By adjusting the solution concentration, diffusible hydrogen atoms that intrude on the steel specimen surface are controlled. The advantage of this solution is the reduced dissolution of a specimen, owing to its high pH of 4 to 5. For comparison, aqueous solutions of HCl for hydrogen charging tests are usually pH 1.

In this study, a quench-tempered martensitic steel was tested. Its chemical composition is Fe–0.21% C–0.22% Si–1.5% Mn–0.06% Ti. The tensile strength of the specimen that was aged at 200 °C was ~1500 MPa. Transmission electron microscopy of the specimen confirmed ε-carbide precipitates. A specimen without tempering was also tested. The HE susceptibility of the specimens was evaluated by the U-bending method with a bending radius of 2~10 mm [20]. The U-bending specimen was 30 mm wide, 100 mm in length, and 1.6 mm thick. An applied stress of 900 MPa was measured by X-ray. The concentration of NH_4SCN was 0.1%. The testing was carried out at room temperature.

Preliminary and qualitative experimental results are presented here. The tempered specimens showed no cracking after immersion for 300 h, whereas the specimens without tempering displayed cracks. Thus, the ε-carbide precipitates lowered the HE susceptibility of the specimens. Hydrogen contents in the tested specimens were measured by thermal desorption analysis with gas chromatography. Figure 1 compares the hydrogen-evolution curves of the quenched and tempered specimens that were charged previously with hydrogen for 100 h at room temperature. The heating rate was 200 K/h. The dotted line represents the evolution curve of the as-quenched specimen. The peak at ~100 °C is ascribed to diffusible hydrogen atoms in the specimen. The solid curve is for the tempered specimen with ε-carbide precipitates. A large peak starts at ~300 and ends at 400 °C. This range corresponds to the decomposition of ε-carbide to cementite in the Fe–C phase diagram. Through the decomposition, the hydrogen atoms trapped in the ε-carbide are forced to the outside of the specimen. Although this experiment is qualitative in nature, the result suggests that hydrogen atoms are trapped strongly at the ε-carbide precipitates. It is believed that once trapped, they will not easily return to diffusible states, which lowers the HE susceptibility.

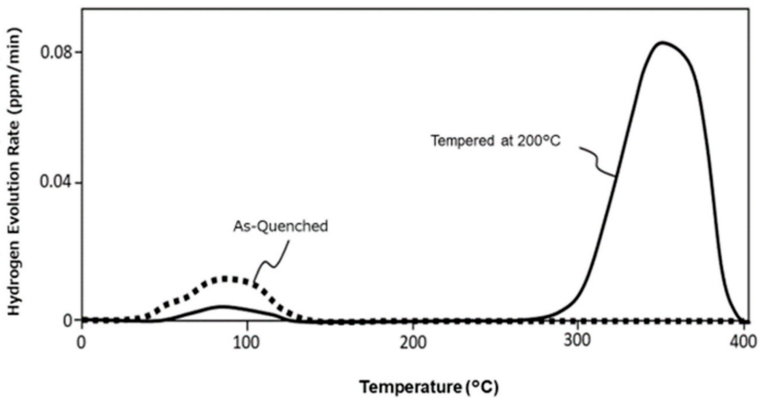


Figure 1. Hydrogen-evolution curves of steel specimens with martensitic structure. The dotted line represents the quenched specimen, and the solid line represents the quench-tempered specimen.

The lattice sites for the hydrogen atoms in ε-carbide will be interstitial and/or substitutional sites in the crystal. In the case of hydrogen-storage materials such $LaNi_5$, the

absorbed hydrogen atoms occupy octahedral and tetrahedral interstitial sites. These sites facilitate easy desorption of hydrogen atoms that are required for such materials. However, for ε-carbide, which may be regarded as a non-stoichiometric compound between Fe_2C (=$Fe_{2.4}C_{1.2}$) and Fe_3C (=$Fe_{2.4}C_8$), vacant substitutional sites in the carbon-lattice are available. If the hydrogen atoms occupy all vacant substitutional sites, the chemical formula is expressed as $Fe_{2.4}CH_{0.2}$, compared with the reported value of $Fe_{2.4}CH_{0.04}$ [9]. The substitutional hydrogen atoms will be stable compared with the interstitial ones. Further studies are needed to determine the full hydrogen-absorption capacity of ε-carbide. Theoretically, ab initio calculations of the trapping energy of hydrogen atoms in the ε-carbide lattice are desirable. Experimentally, the influence of hydrogen absorption on the mechanical spectrum of carbon dipoles in ε-carbide may provide insight into the locations of hydrogen atoms in the ε-carbide lattice [21,22].

4. Heuristic Design of Steels

The literature survey and the experimental studies described above lead to a design of advanced steels with low HE susceptibility. Requirements for this kind of steel are martensitic microstructure with ε-carbide precipitates. The precipitates must be stabilized by alloying and should have a proper shape, size, and dispersion. Some carbides, nitrides, or carbonitrides that may act as the inoculants for ε-carbide have to be discussed. The factors that contribute to the yield strength of martensitic steel have been classified as solid solution strengthening, precipitation or dispersion strengthening, dislocation strengthening, and lath-boundary strengthening [23,24]. In this case, the second to fourth strengthening mechanisms are involved. The coherency and/or semi-coherency of ε-carbide to the host crystal is expected to have a close relationship with the tensile elongation and impact toughness of the steels. Coherence loss with the introduction of fresh dislocations through the punching of dislocation loops may enhance the steel elongation and toughness. This issue is left for further study.

4.1. Alloying Elements

Carbon: The carbon contents are important in martensitic microstructure and carbide precipitation to design advanced steels that are highly resistant to HE with the assistance of ε-carbide. According to an early study [25], the lowest limit for carbon content to observe ε-carbide in the tempered martensite is 0.2%. The other importance of carbon as an alloying element is shown in the relationship between M_s temperature and the chemical composition [26]:

$$M_s\ (^\circ C) = 539 - 423(\%C) - 30.4(\%Mn) - 17.7(\%Ni) - 12.1(\%Cr) - 7.5(\%Mo) \quad (1)$$

where M_s is the martensitic transformation temperature. Equation (1) shows carbon has the most significant effect on M_s temperature. The M_s temperature can neither be increased nor decreased by varying the cooling rate. In contrast, the temperature at which martensitic transformation ends, M_f, is dependent on the cooling rate.

Silicon: Silicon addition to steels shifts cementite precipitation to higher temperature. This results in the stabilization of ε-carbide up to ~400 °C. The mechanism by which silicon retards the cementite precipitation is that the driving force for the precipitation is dramatically reduced when the cementite is forced to inherit the silicon in the parent phase, which is the martensite [27]. There is also evidence that the silicon can enhance the formation of ε-carbide [28]. Silicon addition of more than 0.8% has been used for martensitic steels. Excessive addition of silicon will induce remarkable hardening that is undesirable for industrial production.

Manganese: This element has a serious effect on M_s temperature as shown in Equation (1). One can control the steel M_s by manganese addition.

4.2. Inoculants for ε-Carbide

Inclusions and precipitates in steels as inoculants for phase transformations have attracted much attention for controlling the grain size of ferritic microstructure. Inclusions, such as VN, TiC, TiN, AlN, and Al_2O_3, can stimulate ferrite nucleation in austenite [29]. TiC is reported to act as the inoculant to precipitate ε-carbide in ferrite [12]. In this case, one must look for effective inoculants to precipitate ε-carbide in martensite. Nano–sized carbides, nitrides, or carbonitrides of metals are the candidate inclusions. Two procedures are probable for introduction of the inoculants: static and dynamic procedures. The starting point of the former is interphase precipitation [30–32]. In interphase precipitation, almost equally spaced rows of nanometer-sized carbides are precipitated in the ferritic microstructure during the austenite-ferrite semi-static transformation. If these precipitates survive coarsening and/or dissolution during reheating of the ferritic steel to the austenitic region for subsequent quenching to martensite, they may act as inoculants for the controlled precipitation of ε-carbide during tempering.

Alternatively, the inoculants may be introduced dynamically during the martensitic transformation. The process takes advantage of solubility difference of nitrogen or carbon between austenite and martensite. Nitrides or carbonitrides of aluminum, titanium, and vanadium are promising precipitates. For low-carbon aluminum-killed steels, AlN and MnS are supposed to nucleate heterogeneously at dislocation nodes [33]. In this case, dislocation nodes in the lath martensite are believed to act as nucleation sites. Although the cooling speed is critically important in this procedure, the heat pattern of steels during processing is simple.

5. Conclusions

Many advanced steels have tempered martensitic microstructures. Their mechanical strength is characterized by a fine sub-grain structure with a high density of free dislocations and metallic carbides and/or nitrides. However, their strength for practical use has been limited mostly to below 1400 MPa, owing to delayed fracture caused by hydrogen. A literature survey suggests that ε-carbide in the tempered martensite is effective for strengthening. An experimental survey on hydrogen absorption and hydrogen embrittlement of a tempered martensitic steel with ε-carbide precipitates has revealed its low HE susceptibility. Based on these surveys, martensitic steels with ε-carbide precipitates are proposed. The steels are expected to be highly resistant to hydrogen embrittlement and to have a high strength and toughness. Silicon is the most important alloying element to stabilize ε-carbide. Inoculants are required for controlled nucleation and dispersion of ε-carbide precipitates. Procedures to introduce inoculants in martensitic steels are discussed.

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