The microdopant effects of surfactant elements on structure-phase transitions during the rapid quenched crystallization of Fe-C-based melts

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Abstract. The nature of microdopant effects of surfactant Te and H\textsubscript{2} reagents on structure-phase transitions in rapidly quenched and crystallized eutectic Fe-C-based melts were studied by experimental and computer methods. On the base of results of statistic-geometrical analysis the new information about the structure changes in multi-scaling systems -from meso- to nano-ones were obtained.

1. Introduction.

As physicochemical agent hydrogen causes, first of all, changes in electron structures of metallic systems and also disturbs the initial states of the materials including phase coexistence, modifies the phase transformation processes, initiates “artificial” types of polymorphism. There are chemical reactions of hydrogen atoms with other alloy elements and as a result the changes in the phase composition. There is a high hydrogen sensitivity of the structure and phase stability of transition metals-based alloys. Due to different affinity of hydrogen atom from other components there are possibilities of appearance of different types of solid solution and various inhomogeneities, lost of stability or even decomposition of alloys into separate phases as a result of the hydrogenation.

2. Hydrogen and Te-microdopant treatments

The kinetics of hydrogen combined with Te microdopant impacts on the processes of structure formation at the amorphization of Fe-based alloys while rapid quenching the melts has been studied (Figure 1). It is well known, that hydrogen presence in Fe-based alloys stimulates the phase-structural transformations of martensite types (e.g. $\gamma \rightarrow \epsilon$) with stabilization of the denser hcp-structure in comparison to fcc one. Experimental data about states of a hydrogen atom in Fe-based alloys were obtained in the internal friction measurements of spectra and Snoek-tipe relaxation effect was revealed.

According to analysis of these data the mechanism of H-diffusion is realized by interstitial jumps (from one non-cubic complex site to another one), but the nature of these complexes was not enough clear. There are possibilities of formation of the H-H or H-substitutional atom pairs. However, it is well known, that hydride compounds do not exist in iron-based systems up to very high pressure (of the order of GPa where iron hydride Fe\textsubscript{2}H with hcp-structure has been revealed). This compound decomposes at atmospheric pressure and temperature near 153K, generating $\alpha$-Fe (bcc) grains and H\textsubscript{2}. But at the presence of carbon in iron systems enhancing with doping of surfactant tellurium the
electron density distribution changes and the Fe-H bonds are modified. It favors to local formation of ferritic nanocrystallites with the hydride structure of \( \alpha \)-H short range order (bcc-type!). It was supposed, that subsequent growth of these crystallites would be realized in forms of nanofibers or needles.

![Figure 1. Rapidly quenching process](image)

It was revealed, that the presence of dispersed nanophases predetermines mainly structure scale effects in all concerned systems through their dominant influence on the processes of diffusion and adhesion and, as a result, on the thermal stability of nanostructured phases. The discovered high hydrogen sorption for these states may be explained by the increasing of disconnected bonds in the superficial grain layers. It causes formation of two composition dependent phases in the materials, namely, diluted or clustered hydrogen atoms centered on grain boundaries of such substructures.

3. **MD-simulation**

To develop the conception of a nanophase formation in transition metal based alloys (namely Fe, Ni and Co) after thermal and hydrogen treatments it was necessary to elaborate an effective molecular dynamic simulation model using the precision potentials of atomic interactions. Thus the MD study of H- induced effects in the Fe-C-based amorphous and nanostructured alloys and the detailed identification of the preferable H- states (H+) and positions were performed.

We started from the analysis of diffraction data and results of computer simulation of Fe, Ni, Pd, Fe-B, Pd-Si – systems using appropriate parameterized potential functions of atomic interactions in frames of unified theory of disordered states. Finally, rather successful MD-model was generated to reveal general features of short range order transformations in the processes of melting, crystallization, nano- and amorphous phase formation. The scheme of the model is shown in Figure 2.

It was demonstrated by computer simulation, that melting of metallic system without covalent bonds was realized by converting of local crystalline polyhedrons into non-crystalline ones with predominant five-fold symmetry (mainly of the icosahedral type, e.g. Voronoi \{0-12-0-…\} type of the FCC icosahedron \{0-0-12-0-…\}). The simulated systems with intermetallic compounds (Fe-B, Pd-Si) were “melted” through the analogous transformations of local pure metallic coordination, but in this case some structure motives of intermetallic compounds of corresponding crystalline phases retains (some kind of genesis conserving quasimolecular forms of crystalline Fe\(_3\)C-ordination). It is necessary to note, that according to diffraction data, two different nanophases are discovered in the course of the multi-step crystallization through the intermediate nano- and amorphous phases: one of
them (stage 1) is characterized by the predominant five-fold symmetry of pre-crystallites of a smaller size (less than 10 nm containing near 1000 atoms in grains) and the other formed by crystalline grains of the size of 100 nm by order. Thus above mentioned nano- and amorphous states, similarly to the state of an undercooled liquid, are formed by the general disordered phase with homothetic short range order but differently disposed in the space-time-continuum of the first-order phase transformation in comparison to equilibrium liquid and crystalline phases.

It was established in the computer simulation, that melting and crystallization processes start inside the precursor phase by nucleation of the five-fold coordinated atom groups with dense packing (from 0.74 for fcc to 0.78 for two superposed rings of fife juxtaposed tetrahedral forming icosahedron). According to the results, the intensive hydrogen sorption corresponding to the thermodynamics state of an alloy is initiated by the increasing of concentration of dangling bonds in grain interfaces of the nano-fragments. Domains of two different phases (dilute hydrogen solution or hydrogen clusters) depending on the alloy composition appear on grain faces located at the interfaces.

4. The influence of hydrogenation on structure and properties

There is some difference between the specific volumes of the $\alpha$- and $\gamma$- phases of Fe-based alloys. Therefore, monitoring of stresses induced by hydrogen can be useful to improve the alloy structure and some of its physical properties, for example, relaxation or strengthening. According to metallographic analysis of real Fe-C based alloys the anomalous eutectic crystallization of hydrogenated melts was discovered on the stage of nucleation of eutectic colonies. In this case the crystallization goes through the dominate formation of metastable carbides of the Fe$_3$C type. At the presence of less than 0.007 wt.% Te undercooling increases and carbide phase forming accompanies by disappearance of graphite phases precipitants in the studied specimens. The results of our research are presented in the Table 1.

The hydrogenation process leads to concentration of valence electrons in the vicinities of H-complexes and, as a result, to essential weakening and metallization of atomic bonds of surrounding
Fe-atoms and stabilization of intermediate metastable states without completing of crystallization and grain growth in the regions with high density of vacancies. Moreover, hydrogenation increases densities of electron states (DOS) at the Fermi surface. As a satellite effects, the plastic deformation stress (the shear module C44) decreases and reversible H - embrittlement appears. This is favorable for mechanical treatment the alloys, especially for extruding, pressing and compacting of nanophase powders in industrial sintering processes.

So, it was shown that the nanophase formation and specific thermal sorption of hydrogen rise activation energy of grain growth and, as a result, efficiently stabilizes nanosystem structures. These energy changes are connected with the hydrogen clustering at the boundaries of nanograins which results in the local structure transformations similar to melting through density of vacancies increase. Similarly to the electrolytic hydrogenation the nanocrystalline and amorphous Fe-based alloys are superplastic.

Table 1. The crystallization and structural parameters of graphite, metallic phases, hydrogen concentrations in the specimens and crystallization temperatures.

| Composition | Type of treatment | Graphite | Metal base | H$_2$, cm$^3$/100g | T$_{cri}$, C |
|-------------|-------------------|----------|------------|-------------------|------------|
| A           | - - roset plate   |          | Ferrite, %  | 80-100 3,45       | 1132       |
|             | + - roset. + interdendrite | 25-40 | 95 | 5,63 | 1115 |
|             | - 0,00 roset. - interdendrite | 10-25 | 100 | - | 3,80 | 1100 |
|             | + 0,00 roset. - interdendrite | 5 | 50 | 6,71 | 1090 |
| B           | - - roset. + isolated plate | 80-125 | 30 | 70 | 4,20 | 1145 |
|             | + - roset. - interdendrite | 40-80 | 60 | - | 4,50 | 1120 |
|             | - 0,00 roset. - interdendrite | 10-25 | 90 | - | 6,70 | 1090 |
|             | + 0,00 roset. - interdendrite | 5 | 50 | 1085 |
| C           | - - isolated plate | 80-125 | 100 | - | 4,21 | 1150 |
|             | + - roset. - interdendrite | 90 | 10 | - | 6,75 | 1134 |
|             | - 0,00 roset. + interdendrite | 25-40 | 100 | - | 4,61 | 1125 |
|             | + 0,01 absent | 30 | 70 | 8,12 | 1090 |

Thus, after the hydrogenation treatment defects regions of an alloy segregate with a sharp decreasing of shear modules. The ball milling of a sample is followed by generation of vacancies and results in enhancing of the noncrystalline system metastability. Modifying of Fe-bonds by hydrogen initiates nucleation of icosahedral phases which results in appearance of local deformations and enhancing the metastability.

**Conclusion.**
In conclusion it is necessary to be noted, that mainly due to two facts – the nanophase generation and hydrogen thermal sorption, the potential barriers of grain growth raise and therefore the nanostructure
are effectively stabilized. So the thermally activated hydrogenation is a fine controlling mechanism for
diffusion-annealing processes, for isomer structure transformations during rapid quenching of melts
and for nano-crystallite formation.