

Letter to Editor

ABOUT OXIDE DISPERSION PARTICLES CHEMICAL COMPATIBILITY WITH AREAS COHERENT DISSIPATION /SUB-GRAINS OF BCC-ALLOYS IN Fe – (Cr, V, Mo, W) SYSTEMS

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Abstract

A concept of partial magnetic moments (PMM) of the iron atoms located in the first ÷ four coordination spheres (1÷4 CS) for bcc lattice have been introduced based on analysis of results obtained by quantum-mechanical calculations (QMC) for volume dependence of the average magnetic moment ferromagnetic (FM) Fe. The values of these moments have been calculated for pure bcc Fe and bcc – Fe–Cr alloys. This concept has been used to formulate a three-sub-lattice model for binary FM alloys of the Fe–M systems (M is an alloying paramagnetic element). Physical reason for sign change dependence of the short-range order and mixing enthalpy obtained by QMCs for Fe–(Cr, V) bcc phases has been found. Using this model it has been predicted that static displacements of Fe - atoms in alloy matrix increase with increasing the of CS number and result in reducing of the area of coherent dissipation (ACD) size with growth of the dimension factor (DF) in the Fe–(Cr, V, Mo, W) systems in agreement with the X-ray experiments. It has been shown theoretically that anisotropy of spin- density in bcc lattice Fe and DF in binary Fe – (Cr, V, Mo, W) systems is main factor for origins of segregations on small angle boundaries of ACD and sub-grains boundaries To prevent the coagulation of both ACD and sub-grains, and to increase the strength of alloys, it is advisable to add oxide dispersion particles into ferrite steel taking into account their chemical compatibility and coherent interfacing with the crystalline lattice of a ferrite matrix. Application of phase diagrams for binary and ternary the Fe–(Y, Zr)–O systems to verify chemical compatibility of oxide dispersion particles with ferrite matrix have been discussed

Keywords: Anisotropy of spin-density; ferritic steels; dimension factor; segregations on grain borders; chemical compatibility; phase diagrams; coherency oxide segregations and bcc-matrix; Fe–Cr–(Mo,W); Fe–Y–O; Fe–Zr–O

1. Introduction

The problem of The Fe-Cr alloys with bcc structure are a base for ferritic steels and they have practical interest as material for shells for nuclear breeder reactors. Ferritic steels demonstrate higher radiation stability in reactor conditions at the temperature 600-900 K in comparison with austenitic steels. It is shown [1] that in comparison with ferrite steel austenitic steels at the temperature above 873 K possess a raised ability to diffusion that results in raised creep of austenitic steels working in condition of the irradiation. In addition, induced activity of alloying elements, which are constituents of austenitic steels (10% Ni), unlike the alloying elements of ferritic steels (Cr) approximately in 100 times longer remain active during storage time. Also, the induced activity of the nickel in comparison with iron, the major element of steel, lasts about 10 times longer. Due to these two mentioned reasons ferritic steels have an essential advantages in comparison with austenitic steels as well as nickel-

based refractory alloys in work under higher temperature (over 873 K) [2]. From comparison of temperature dependences of tensile strength for different steels and nickel based alloys [2] one can conclude that ferritic steel (grade P91 and MANET II) in the temperature range of 873 – 973 K posses for approximately 40% higher strength than austenitic steel and have 2-3 times higher strength than the nickel based alloys. The purpose of this work is searching for the possibility of the Fe-Cr base steels modification by alloying them with small amount of additives such as Mo or W and by using oxide dispersed particles to provide chemical compatibility and coherency with ferritic phase simultaneously. This should prevent size increase of matrix sub-grains.

2. Influence of anisotropies to spin-density on arising the short-range order

In order to achieve the understanding of the reasons for the arising of the short-range order in the

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Fe-base alloys from Fe-Cr system, which was established experimentally [3-4], recently quantum-mechanical calculations of chemical composition dependence from mixing enthalpy were carried out for the main ferromagnetic state of alloys [5-6] and sign change dependence was found. These results indicated stabilization of ferromagnetic bcc-Fe-Cr alloys. However, in works [5-6] a physical reason for presence of the short order in these alloys was not shown. In work [7] based on the results of quantum-mechanical calculations of the average magnetic moment for ferromagnetic (FM) iron as a function of the volume the partial magnetic moments of the iron atoms located in the first four coordination spheres (CS) were introduced. An extended cell, containing 8 bcc cells including 16 atoms, located on the $1\div 4$ CS relative to the center of the extended cell was considered in [7]. It was also shown in [7] that calculated values of partial magnetic moments of Fe-atoms, located in $1\div 3$ CSs, qualitatively agrees with spin-density depending on distances in crystallographic directions type $\langle 111 \rangle$, $\langle 100 \rangle$ and $\langle 110 \rangle$ accordingly to experimentally determined magnetic moments distribution in bcc lattice [8]. Within the framework of Inden-Hillert-Jarl formalism of the magnetic contribution into the Gibbs energy description it was shown [7] that the anisotropy of spin-density in the bcc-Fe was responsible for location arrangement impurity atoms in the first and second CSs in alloys of the Fe-Cr [3-4] and Fe-V systems [9]. In crystallographic direction $\langle 110 \rangle$ static displacements of Fe-atoms, located in 3CS in extended cell, containing impurity atom at center will be situated in specified direction. The static displacements of Fe-atoms from sites of average (ideal) of the crystalline lattice inside extended cell with impurity atom in its center will generate the field of the elastic stresses, which results partial suppression of partial magnetic moments of Fe atoms.

At location of the impurity atom in the centre of the extended cell, see Fig.1, presence of the dimensioned factor results in arising of static Fe atoms displacements, located in different coordination spheres (CS). The vector summa of static displacements vectors of Fe atoms in the first CS, results in increasing the of static displacements module of Fe atoms in second CS, in $(4/\sqrt{3}) \approx 2.3$ times more in comparison with module of vectors of static displacements of Fe atoms in first CS in $\langle 111 \rangle$ type directions. Presence of one impurity atom in one extended cell corresponds to the concentration an alloy, equals 0.0625 mole fraction. At concentration of 2nd component less 6.25 at.% some nearby extended cells relative to the extended cell containing one impurity atom will not contain the impurity atoms. It was shown that difference in values of linear thermal expansion coefficients of Fe and Cr equal to

12×10^{-6} and 6×10^{-6} , respectively leads to vanishing of lesser dimension factor in the system Fe-Cr at temperatures around 1000 K. That is why the alloying of Fe-9Cr alloy by Mo and/or W having larger dimension factor make it possible to get single phase alloys of compositions Fe-(8-12 at.%) Cr-(0.2at.% W/1at.%Mo) in the 773-973 K. Phase diagrams of the Fe-Cr-Mo and Fe-Cr-W systems calculated based on thermodynamic data [10] are presented in Fig 2 and 3. Calculations at 873 K show that maximal solubility of Cr in Fe based bcc phase is 20 at.% in both systems, while maximal solubility of W is substantially lower (0.2 at.%) than for Mo (1 at.%).

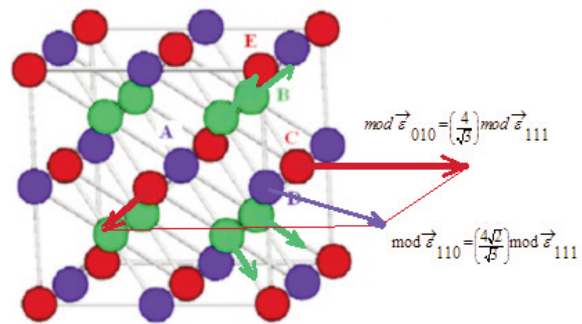


Figure 1. The influence of the dimensioned factor on static-displacements of Fe atoms, located on the first (green), second (red) and three (blue) coordination spheres relatively center impurity atom, located in point A, for binary Fe- (Cr, V, Mo, W) alloys with concentration equals 0.0625.

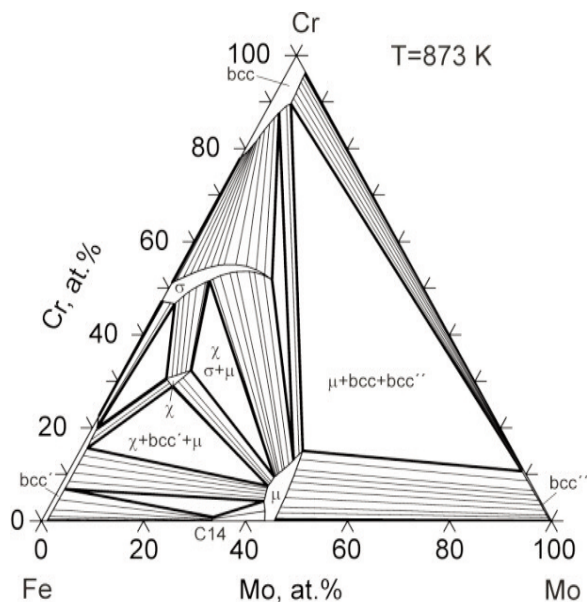


Figure 2. Isothermal section of Fe-Cr-Mo system at 873 K calculated using database from Ref [12]. Considered phases are bcc, fcc, C14 (Laves phase), χ , μ and σ .

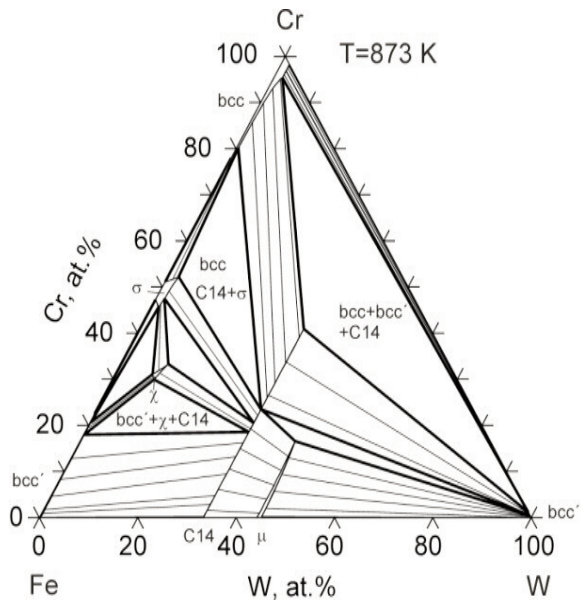


Figure 3. Isothermal section of Fe–Cr–W system at 873 K calculated using database from Ref [12]. Considered phases are bcc, fcc, C14 (Laves phase), χ , μ and σ .

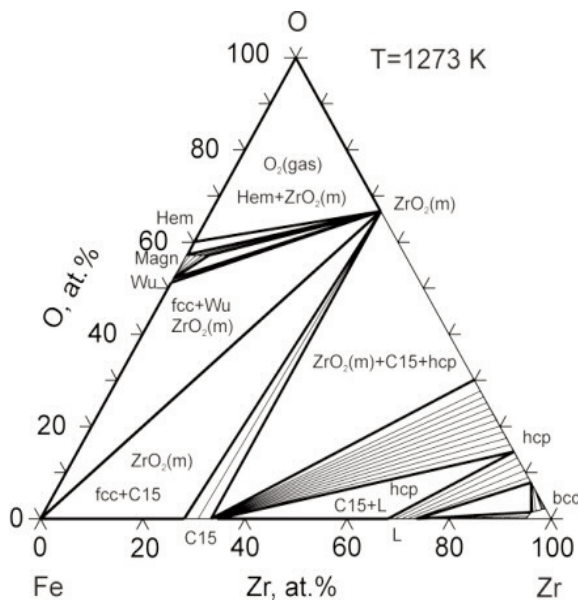


Figure 4. Calculated phase diagram of the Zr–Fe–O system based on thermodynamic data [10]

3. Oxide Dispersion Strengthened (ODS) ferrite steels.

To keep constant the sizes of coherent scattering blocks and sub-grains as well as to prevent coagulation of grains and their growth when alloys is used at temperatures $T/T_{\text{melt}}=0.5-0.6$ it is appropriate to introduce a dispersed particles with the structure coherent with bcc lattice. These particles should have

high enthalpy of formation. In particular oxides of yttrium and titanium can be used for this purpose to create ODS ferrite – martensitic steel. It can be seen that Y_2O_3 is in equilibrium with Fe fcc phase [13]. Therefore Y_2O_3 with cubic structure is chemically compatible with fcc phase as well as with bcc Fe-based phase which is stable at temperatures below 912°C . Actually, according to phase diagram presented in [13] the Y_2O_3 cubic phase can be in equilibrium with Y_2Fe_{17} and Fe (fcc or bcc), only with Fe (fcc or bcc) or with Fe and $FeYO_3$ (perovskite) phase. Therefore compatibility of Y_2O_3 with iron depends on partial pressure of oxygen. At present there are no data showing partial pressures at which three phase assemblages $Fe+Y_2O_3+FeYO_3$ and $Fe+Fe_xO(\text{wustite})+FeYO_3$ are stable and in which range of $P(O_2)$ two-phase assemblage $Fe+Y_2O_3$ is stable. Additionally, the influence of Cr alloying of Fe based fcc phase to phase relations with Y_2O_3 is not known. Since Cr has also several stable valence states, this will make phase relations and partial pressures even more complicated. Another compound which lattice can be coherent with Fe-Cr bcc lattice is Y_2O_3 stabilized ZrO_2 with fluorite structure. The thermodynamic database for the Zr-Fe-O system was derived based on phase equilibria in ZrO_2 -FeO- Fe_2O_3 system and combined with binary systems descriptions. The phase diagram of the Zr-Fe-O system calculated at 1273 K based on thermodynamic description [10] is presented in Fig. 4. Phase diagram shows that Fe can be in equilibrium with monoclinic ZrO_2 phase.

Calculations indicate range of oxygen partial pressures ($\lg P(O_2)$ in bar) where two phase mixture $Fe+ZrO_2$ is stable. The range of $\lg P(O_2)$ is between -32.22 (equilibrium $C14+fcc+ZrO_2$) and -14.87 (equilibrium $fcc+ZrO_2+\text{wustite}$) at 1273 K. At higher partial pressure of oxygen $\lg(P(O_2))>-14.87$ $ZrO_2(m)$ will be in equilibrium with wustite. Calculations at lower temperature show chemical compatibility of ZrO_2 with Fe bcc phase. For example, at 1173 K the range of stability of $bcc+ZrO_2$ phases assemblage is calculated as $\lg P(O_2)$ in the range between -35.7 and -16.7 . Phase diagram of ZrO_2 - Y_2O_3 system was investigated by many researches experimentally and theoretically. Phase diagram of this system calculated based on data [11] is presented in Fig.5

This diagram shows that ZrO_2 with fluorite structure can be stabilized by Y_2O_3 in the wide range of temperature including 1273 K and below. Therefore based on phase diagrams presented in Fig. 4 and it can be assumed that cubic ZrO_2 phase should be compatible with Fe bcc phase at temperatures below 1185 K. It is possible to conclude that ZrO_2 stabilized by Y_2O_3 with fluorite structure coherent with bcc lattice is good candidate material for ODS ferrite steels.

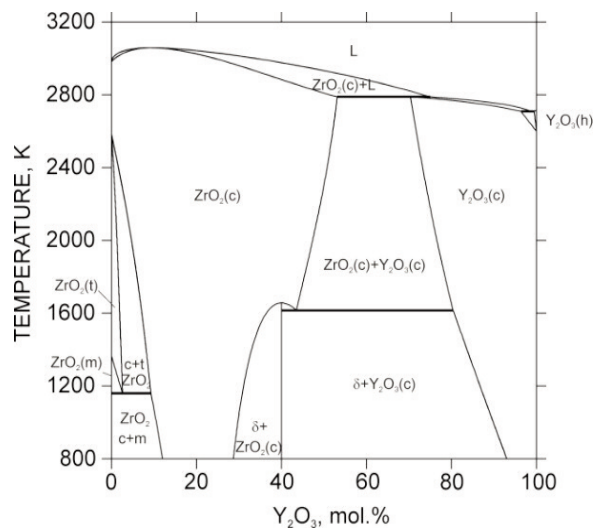


Figure 5. Calculated phase diagram of the ZrO_2 - Y_2O_3 system calculated based on thermodynamic data [11].

4. Conclusion

Application of phase diagrams for binary and ternary as metallic Fe-Cr-(Mo, W) systems as well for as oxide the Fe-(Y, Zr)-O systems to verify chemical compatibility of oxide dispersion particles with ferrite matrix have been proposed and discussed.

Acknowledgements

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