ELECTRONIC STRUCTURE OF Fe – C MELTS ALLOYED WITH VANADIUM

M. P. Dovgopol, S. P. Dovgopol, I. Z. Radovskii, and P. V. Gel'd

The electronic structure of Fe–V–0.2% C and Fe–V–1% Mn–0.2% C melts containing 0 to 0.4% C is discussed on the basis of the results of an investigation of the magnetic susceptibility. It is suggested that the vanadium atoms are in an impurity state in the iron–carbon matrix and that quasi-stationary d-levels of the impurity atoms are formed, as in the Anderson model.

1. In engineering today wide use is made of structural steels alloyed with vanadium, whose physical and mechanical properties are largely determined by the electronic structure, which has been quite inadequately investigated. Since the special features of the electronic structure of metals and alloys are manifested in the most direct form in the liquid phase (owing to the absence of complications due to lattice anisotropy, presence of intercrystalline boundaries, etc.) it is of interest to investigate the physical properties of Fe–V–C melts.

In the present work we investigated the magnetic susceptibility of alloys containing 0.2% C and 0.05, 0.15, 0.25, 0.35, and 0.45% V, and also similar preparations containing 1% Mn (weight percentages are indicated throughout). It should be noted that the magnetic susceptibility of such alloys at high temperatures has not been investigated before. To prepare the specimens we used mark V-3 carbonyl iron, spectrally pure graphite, metallic vanadium (99.98% V), and electrolytic manganese. From them we first smelted an iron–vanadium alloy (46.7% V), which was then crushed and mixed in the necessary proportions with the alloying additives. The mixture obtained in this way was pressed into briquets (20–30 g) under a pressure of 500 kg/cm² and remelted in an argon atmosphere in a MVP–3M vacuum induction furnace. The composition of the preparations was checked by chemical analysis.

The magnetic susceptibility χ was investigated by the Faraday method in the temperature range 900–1800 °C on the apparatus described in [1]. The error of measurement did not exceed ± 4%.

2. As in the case of Fe–C melts [2], the investigated materials did not conform to the Curie–Weiss law, which indicates that the experimental data cannot be interpreted on the basis of a model of localized (on Fe sites) spin magnetic moments. A more accurate picture is that developed in [3] for pure liquid 3d transition metals (extended in [2–4] and [14] to Fe–C, Fe–Mn–C, and Fe–Mn melts), according to which the magnetic susceptibility is proportional to the density of states on the Fermi level D(E_F), which depends, in turn, on the concentration χ of alloying elements. We note that this model is not equivalent to the usual band theory of Pauli paramagnetism, since the strong interaction of collectivized 3d electrons with the transition-metal ions is taken into account. According to this model, the introduction of the alloying element leads to a change in electron concentration in the 3d band of the alloy either by simple substitution of iron atoms or by the formation of covalent-metallic bonds between the atoms of the alloying element and carbon atoms, accompanied by the rupture of the corresponding bonds between iron and carbon atoms. Some of the iron 3d electrons localized in the (Fe–C) bonds are released in this case, which leads to an increase in electron concentration in the 3d band and to a shift of the Fermi level towards higher energies. In fact, the two indicated mechanisms operate simultaneously, but the contribution of each of them depends on the concentration of alloying elements. In particular, this accounts for the special features of the relation χ(x_mn) in alloys of the Fe–Mn–C system [4].

3. As distinct from manganese, the number of 3d electrons in vanadium is much smaller than in iron [13]. In this case it is probably more appropriate to adopt the approach in which the vanadium atoms are regarded as an impurity with good localization of the d states, whose interaction with the alloy d-band electrons

is a perturbing factor [5-8]. As a result the localized level becomes quasi-stationary with width

$$\Delta \Gamma = \pi <|V_{dk}|^2>_{E_F} D(E_F),$$

where $V_{dk} = \langle \hat{d}\hat{V}|\kappa \rangle$ is the matrix element of the operator of the interaction that "mixes" the localized $d$ states with the conducting states, which are characterized by a wave vector $\kappa$; $\langle \ldots \rangle_{E_F}$ means averaging over the Fermi surface.

It was shown in [7, 8] that the quasi-stationary level can be split into sublevels $d_+$ and $d_-$ with different energies ($E_{d_+}$ and $E_{d_-}$) and different populations ($n_{d_+}$ and $n_{d_-}$) if the condition

$$U > \Delta \Gamma,$$

is fulfilled, where $U$ is the energy of Coulomb correlative interaction of electrons with different spin orientation on the impurity $d$ level.

As a result of moment $\mu_B (n_{d_+} - n_{d_-})$, where $\mu_B$ is the Bohr magneton, is located on the impurity node.

For vanadium $U \approx 2$ eV [9]. The density of states on the Fermi level does not differ greatly in liquid iron and in an Fe-0.2% C alloy [2], which allows us to use the tentative value for liquid iron: $D(E_F) \approx 2$ eV$^{-1}$ [10].

Using these values we find from Eqs. (1) and (2) that a magnetic state arises on vanadium atoms in (Fe-V-C) melts when

$$\sqrt{<|V_{dk}|^2>_{E_F}} < 0.5 \text{ eV}.$$  

It was shown in [7] for the case of $(s-d)$ interaction, when the Bloch $\kappa$ states belong to the $s$ band of the alloy, that $|V_{dk}| = 2$ eV.

In our case, however, the collectivized $\kappa$ states contain a considerable admixture of iron $d$ states, which are better described in the strong-coupling approximation [10] with a small overlap of the orbitals of neighboring nodes. In view of this we can expect a reduction of the matrix element $|V_{dk}|$ here. It is important to note that for dilute solid solutions of vanadium in iron there is experimental corroboration [12] of the existence of a local magnetic moment ($\approx 0.9 \mu_B$) on vanadium atoms. This indicates that condition (3) may be fulfilled here. However, owing to the relatively small value of $|V_{dk}|$ it is fulfilled "at the limit" and can be violated when there is a relatively small intensification of $(d-\kappa)$ interaction.

4. In the light of the above ideas (single $d$-band model, Sec. 2 and the localized impurity state model, Sec. 3) we now consider the special features of the isotherms of the magnetic susceptibility $\chi(x_V)$ for the Fe-V-0.2% C and Fe-V-1% Mn-0.2% C melts shown in Fig. 1. It is apparent first of all that the magnetic susceptibility attains a maximum at vanadium concentration $x_{V_c} = 0.35\%$. This fact could be attributed,