SELF-DIFFUSION OF V-48 IN THE FeV σ-PHASE
AND IN AN Fe-47 wt.% V SOLID SOLUTION

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Self-diffusion coefficients of vanadium in the FeV σ-phase and in the corresponding α-solid solution (Fe-47 wt.% V) measured in the temperature ranges 1002–1115 °C (σ-phase) and 1230–1320 °C are reported. The found results differ fundamentally and significantly from the relations in ordered and disordered solid solutions [9]. The diffusivity in σ-phase at the transition temperature \( T_{σ/α} = 1200 °C \) is cca 14 times lower than the diffusivity in the b.c.c. solid solution, the chemical composition of which is the same. The lowering is caused by the different values of frequency factors, \( D_0σ = 0.11 \text{ cm}^2/\text{s} \) and \( D_0α = 45 \text{ cm}^2/\text{s} \). The effect of the corresponding activation enthalpies \( H_σ = 252 \text{ kJ/mole} \) and \( H_α = 293 \text{ kJ/mole} \) is small and quite opposite. The occurrence of higher activation enthalpy \( H_α \) in the α-solid solution at temperatures \( T > T_{α/σ} \) may be attributed to a certain amount of the f.c.c. phase coexisting in the b.c.c. matrix at concentrations \( c_ν > 27 \text{ wt.%} \) at sufficiently high temperatures [7]. A comparison of vanadium self-diffusion characteristics measured in the σ-phase to the extrapolated values obtained on the basis of the previous measurements [1] in the Fe-V primary solid solutions \( α_1 \) shows that the diffusivity ratio \( D_α/α_1 (1473 \text{ K}) \approx 33 \) and that the activation enthalpy \( H_α \) is by about 3% higher than the values \( H_α/α_1 \) (eq. (5)) measured in the uniphase b.c.c. solid solutions.

I. INTRODUCTION

The results of the vanadium self-diffusion measurements in the α-solid solutions of the Fe-V system in the entire concentration interval and in the temperature range 839 to 1320 °C were formerly published [1] by Obřtlik and Kučera. The same authors alone [2], and together with K. Ciha [3], also published the results concerning Fe-59 self-diffusion in the FeV system. In the quoted paper [1] it has been shown that the measured diffusion characteristics can be divided into two sets: The first set — corresponding to the primary Fe-V b.c.c. solid solutions (0 to 28 wt.% V) — and the second one — relevant to the V-Fe solid solutions (47 to 100 wt.% V). The first set of experimental data \( D_αα_1 \) and \( H_αα_1 \) yielded the concentration and temperature variation of the V self-diffusion coefficient expressed by the relation

\[
D_{α_1} = (2.044 \pm 0.074) \exp \left\{ -\left[ (229.8 \pm 0.4) + (0.321 \pm 0.027) c_ν \right] / RT \right\}.
\]

In the second concentration interval corresponding to the V-Fe primary solid solutions [4], the equation

\[
D_{α_2} = \exp \left\{ - (34.0 - 1.190 c_ν + 10^{-3} \times 8.345 c_ν^2) \right\} \times \\
\times \exp \left\{ - (217 + 15.54 c_ν - 0.1016 c_ν^2) / RT \right\}
\]
was found to be valid. The different concentration dependence of $D_0(c_V)$ and $H(c_V)$ in eqs. (2) and (1) were attributed partly to the occurrence of atomic ordering [5, 6] and partly to some amount of the f.c.c. phase [7], coexisting with the b.c.c. phase in the Fe-V matrix at high temperatures and at high V content. We may recall [7] that the Fe-V solid solutions (25-5 – 72 wt.% V) contain, after quenching from the temperatures 1400, 1300, 1200 and 1150°C, some amount of the f.c.c. phase which is dispersed in the b.c.c. matrix. The content of the f.c.c. phase is increasing from 5% (at a composition of 28.5 at.% V) to 80% (at 74% V).

The aim of the present paper is to complete the previous results [1 – 3] by the V self-diffusion measurements in the Fe-V σ-phase previously reported in [8], to compare them to the self-diffusion in Fe-V solid solutions, to point out some peculiarities of these results with respect to the diffusion in ordered Cu-Zn solutions [9], and to present a correlation between the activation enthalpy $H(c_V)$ and microhardness values measured on the individual Fe-V alloys.

II. EXPERIMENTAL

The σ-phase samples were prepared in the Research Institute of Materials (SVÚM Praha) using a procedure developed and described in the research report [10]. Spectral pure iron J. M. (catalogue No. JMC 848) and vanadium (No. JMC 579) were used as charge materials. The individual melts were carried out in a vacuum arc furnace (Heraeus L 200 h). First, the disc-shaped ingots were melted in a water-cooled copper mould. These ingots were several times converted and remelted to get a composition, as homogeneous as possible. Further, the homogenized samples were put on the orifice of another massive copper mould and remelted. This operation made it possible to get the ingots in a cylindrical form and in a rather segregation-less state. Each ingot was cut into individual diffusion samples (four pieces from each ingot) and their homogeneity was verified by specific mass measurements. It was confirmed that the discrepancies were lower than ±0.02 g/cm³, which amounts to about 0.5%. The cut samples were sealed into evacuated ampules and heated at 750 °C for 430 hours to obtain a σ-phase, reasonably homogeneous. The submicrostructure of the FeV σ-phase is claimed by [4] to be, similarly to βU, tetragonal with the lattice parameters $a = 8.95$ Å, $c = 4.62$ Å and with 30 atoms per unit cell. A tentative atomic model of this structure was published in Structure Reports [11]. According to [11] the σ-phase structure is essentially a layer structure with nearly flat layers at $z = 1/4$ (B layer) and $z = 3/4$ (C layer) separated by A layers at $z = 0$ and 1/2, giving a stacking order of ABACABAC…. The atoms in the A-type layer are located cca $1.39 \times 10^{-10}$ m above and below the unoccupied centres of the hexagons in the B- and C-type layers. Interatomic distances between the A-atoms and six corners of the hexagons vary from $3.03 \times 10^{-10}$ to $3.30 \times 10^{-10}$ m. Each A-atom has 14 nearest neighbours, atoms in the B or C layers have either 12, 12 or 15 neigh-