



Mössbauer spectroscopic study of a σ -Fe_{65.9}V_{34.1} alloy: Curie and Debye temperatures



Jan Żukrowski^a, Stanisław M. Dubiel^{b,*}

^a AGH University of Science and Technology, Academic Center for Materials and Nanotechnology, al. A. Mickiewicza 30, 30-059 Kraków, Poland

^b AGH University of Science and Technology, Faculty of Physics and Applied Computer Science, al. A. Mickiewicza 30, 30-059 Kraków, Poland

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ABSTRACT

Sigma-phase Fe_{65.9}V_{34.1} alloy was investigated with the Mössbauer spectroscopy. Mössbauer spectra were recorded in the temperature interval of 80–330 K. Their analysis in terms of the hyperfine distribution protocol yielded the average hyperfine field, $\langle B \rangle$, the average center shift, $\langle CS \rangle$, and the spectral area, A. The magnetic ordering temperature, $T_C = 312.5(5)$ K was determined from the temperature dependence of $\langle B \rangle$, and the Debye temperature, T_D , from the temperature dependence of $\langle CS \rangle$ and the relative spectral area. The value obtained from the former was 403(17) K and that from the latter 374(2) K. The lattice dynamics of Fe atoms was described in terms of the kinetic, E_k , and the potential energy, E_p . The force constant for the Fe atoms vibrations was determined as 188 (6) N/m.

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1. Introduction

Sigma (σ) phase belongs to the Frank-Kasper (FK) family of phases which are also designated as topologically close-packed (TCP) structures. Their characteristic features are high values (12–16) of coordination numbers [1]. An interest in σ (and other FK-phases) is twofold: on one hand it has practical reasons, and, on the other hand, scientific ones. The former interest stems from the detrimental effect of σ on many useful properties of technologically important materials e. g. steels, super alloys, high entropy alloys. Its presence, even in low percentage, significantly deteriorates useful properties like mechanical strength and resistance to high temperature corrosion e. g. Ref. [2]. In these circumstances, the interest in σ from the practical viewpoint is rather concentrated on efforts aimed at development of such materials in which its precipitation is suppressed or, at least, retarded. The scientific interest in σ is challenged by its complex crystallographic structure (tetragonal unit cell – space group $D^{14}_{4h} - P4_2/mnm$ – with 30 atoms residing on 5 non-equivalent lattice sites), and interesting physical properties. They can be readily tailored by changing alloy elements and chemical composition thanks to the fact that σ can exist in a

certain composition range. Concerning magnetic properties of σ in the Fe–V system, one of the subjects of the present study, they were revealed in early 1960s [3], and until recently regarded as ferromagnetic. Not long ago, its magnetism was shown to be more complex than believed viz. it had turned out to have a re-entrant character [4]. The Fe–V system is especially interesting with regard to σ , as the phase can be formed within a wide range of composition viz. ~33 – ~65 at% V [5]. This gives a unique opportunity for changing physical properties of σ in a wide range of composition. Concerning the magnetic ones, the magnetic ordering temperature (Curie point), T_C , can be continuously raised up to above room temperature. The actual record obtained for the Fe_{65.6}V_{34.4} alloy is as high as ~307 K as determined from magnetization measurements and ~324 K as found from Mössbauer spectroscopic study [6].

Regarding the Debye temperature, T_D , of the σ -Fe_{100-x}V_x alloys ($34.4 \leq x \leq 59$) so far it was determined only with the Mössbauer spectroscopy from a temperature dependence of the center shift [7]. The T_D -values span between ~420 and ~600 K and do not show any monotonous behavior.

This paper reports results on the Curie and Debye temperatures as determined using the Mössbauer spectroscopy on a σ -Fe_{65.9}V_{34.1} sample which, to our best knowledge, is the σ -FeV alloy with the lowest concentration of V investigated so far.

* Corresponding author.

E-mail address: Stanislaw.Dubiel@fis.agh.edu.pl (S.M. Dubiel).

2. Experimental

2.1. Sample preparation and characterization

Master alloy of a nominal composition α -Fe_{66.5}V_{33.5} was prepared by melting 1323 mg of Fe (99.95% purity) and 609 mg of V (99.5% purity) in an arc furnace under protective argon atmosphere. A loss of mass caused by the melting was 2 mg which corresponds to an uncertainty in the concentration of ± 0.1 at%. The ingot was flipped over and remelted three times before it was solution treated at 1273 K for 72 h to increase its homogeneity. Finally, it was quenched onto a block of brass kept at 295 K. The transformation into the σ -phase was performed by annealing the solution-treated ingot at $T = 973$ K for 14 days. The verification of the α -to- σ phase transformation was done on a powder sample by recording a room-temperature X-ray diffraction pattern – shown in Fig. 1 – using Cu-K α radiation ($\lambda = 1.54053$ Å) and an Empyrean X-ray diffractometer from PANalytical. Its analysis with the FullProf software gave evidence that the master alloy was transformed into σ to 97.5(5)%. The untransformed residual phase (2.5%) was identified as α -iron. Thus the stoichiometry of σ can be estimated as Fe_{65.9}V_{34.1}. The parameters of the unit cell of σ were found to be as follows: $a = 8.8674(5)$ Å and $c = 4.6015(4)$ Å. They are in line with those found previously for the alloys with higher contents of vanadium [7].

2.2. Mössbauer spectra measurements and analysis

Mössbauer spectra were recorded in a temperature range of 80–330 K using a standard spectrometer working in a constant acceleration mode. Gamma rays of 14.4 keV were supplied by a ⁵⁷Co source embedded into a Rh matrix. Examples of the spectra are presented in Fig. 2 (left panel). They are very similar in shape to those recorded previously on the σ -Fe_{65.6}V_{34.4} alloy [6]. The spectra were analyzed to yield spectral parameters pertinent to two quantities of interest viz. the magnetic ordering temperature (Curie), T_C , and the Debye temperature, T_D . The former can be readily determined from a temperature dependence of the average hyperfine field, $\langle B \rangle$, while the latter in two ways: from a temperature dependence of (a) the center shift, CS, and (b) relative recoil-free fraction, f/f_0 .

Mössbauer spectra were analyzed using a least-square procedure and the transmission integral approach. All three hyperfine interactions were taken into account. Each spectrum was assumed

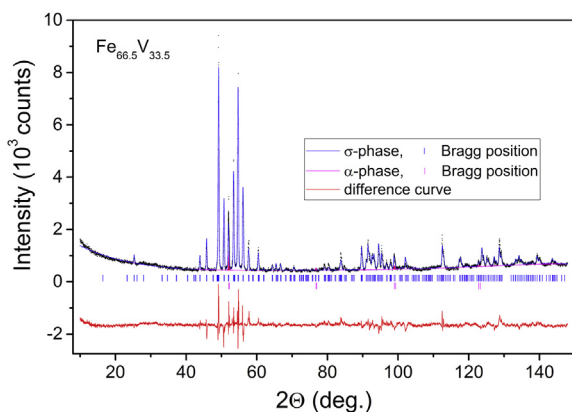


Fig. 1. The Rietveld refinement XRD pattern of Fe_{66.5}V_{33.5} alloy recorded at room temperature. Positions of peaks of the σ and α phases are indicated by vertical bars in black and red, respectively. A difference curve between the measured and the calculated patterns is also displayed. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

to be composed of five components (sub spectra) following the fact that Fe atoms occupy all five lattice sites in the unit cell of σ . The shape of each component was assumed to have the Voigt's profile [8]. Relative contributions of the components, W_k , were equal to the corresponding relative lattice site occupancies by Fe atoms as revealed from the neutron diffraction experiment [9]. They were kept constant in the fitting procedure. A center shift, CS_k , ($k = 1, 2, 3, 4, 5$) of each component was a sum of the isomer shift, IS_k , characteristic of a given component (sub lattice) as reported elsewhere [10], and the so-called second order Doppler shift, SOD . The latter was common to all five components and treated as free parameter. The temperature dependence of the isomer shift is very weak [11], so it was neglected. Consequently, the entire temperature dependence of the center shift was ascribed to the temperature dependence of SOD . The latter can be used to determine the Debye temperature and the mean-square velocity of lattice vibrations – see Section 3.2.

Magnetic properties of the particular lattice sites in the σ -FeV alloys (and other σ -phase alloys) have not been fully resolved yet. However, theoretical calculations [12] and ⁵¹V NMR measurements [13] gave evidence that all five sub lattices contribute to the magnetism. Therefore, we assumed that each of the five components adds to the average hyperfine field, $\langle B \rangle$. The Gaussian distribution of the hyperfine field was assumed, and $\langle B \rangle$ was obtained by integrating the five Gaussians. Examples of the hyperfine distribution curves received in this way are shown in Fig. 2, and the best-fit spectral parameters are displayed in Table 1.

3. Results and discussion

3.1. Curie temperature

Temperature dependence of $\langle B \rangle$ is illustrated in Fig. 3. Two sets of data are displayed: (a) the presently measured ones, and (b) those reported in Ref. [6]. Both sets of the data were analyzed in terms of the Brillouin function. The best fit to the present data was achieved with the total angular momentum quantum number $J = 3$ and yielded the magnetic ordering temperature of $T_C = 312.4(5)$ K. The extrapolated to zero temperature value of $\langle B \rangle = 12.07(5)$ T is equivalent to the magnetic moment of $0.9 \mu_B$ using the conversion constant reported elsewhere [6].

It is evident from Fig. 3 that the $\langle B \rangle(T)$ dependence as found in the present study is different than the one obtained for the σ -Fe_{65.6}V_{34.4} alloy [6]. The largest difference exists in the value of T_C which for the presently studied sample is by ~ 12 K lower. Another difference occurs in the temperature interval of ~ 80 – 200 K in which the presently determined values of $\langle B \rangle$ are higher than the corresponding ones reported previously [6]. There is also a difference in the value of J which in the case of the σ -Fe_{65.6}V_{34.4} sample was equal to 3.5. The differences in the $\langle B \rangle(T)$ behavior can be understood in terms of a different (a) concentration of V, (b) degree of chemical homogeneity, and/or (c) site occupancy in the two alloys. The (b) and (c) effects can have its origin in various conditions applied for the $\alpha \rightarrow \sigma$ phase transformation. Following the $T_C(x)$ – relationship for the σ -FeV alloys viz. an increase of T_C at the rate of ~ 10 K per at% Fe in the range of ~ 34.4 – 40 at% V [6], one would expect $T_C \approx 325$ K for the σ -Fe_{65.9}V_{34.1} alloy, whereas $T_C = 312.5$ K was presently determined from the $\langle B \rangle(T)$ plot. The Mössbauer spectroscopy, being a microscopic method, gives information on local atomic configurations usually within the radius of two neighbor shells around the probe nuclei. Therefore, spectral parameters including the hyperfine field may have different values for samples having different degree of the homogeneity and/or variations in the lattice sites occupancy. On the other hand, magnetization, M , as a macroscopic method is much less, if ever, sensitive to

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