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Structural stability of the sigma phase FeCr under pressure up to 77 GPa

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Abstract

A tetragonal σ phase of the equiatomic FeCr alloy was investigated by x-ray diffraction under pressure up to 77 GPa. The phase was found to be stable in the whole pressure range studied. The equation of state for the tetragonal phase was found to have a value of bulk modulus $K_0 = 217(5)$ GPa and its pressure derivative was $K'_0 = 5.8(2)$, which makes it less compressible than the constituent elements. Electronic factors governing the σ phase stability are discussed in relation to the Hume-Rothery mechanism.

1. Introduction

Fe-based alloys are important for the technology of steel production and for geosciences with respect to the Earth's core. The Fe–Cr alloy system, with both constituent elements crystallizing in a body-centered cubic structure, contains an intermediate phase of the nearly equiatomic composition with a complex crystal structure. The structure of this phase, called the σ phase, is tetragonal with 30 atoms in the unit cell, space group $P4_2/mnm$, lattice parameters $a = 8.7995$ Å, $c = 4.5442$ Å, $c/a = 0.517$, Pearson symbol $tP30$ [1]. The σ phase occurs in a number of binary and ternary systems involving transition-group elements [2]. This structure has been found in two pure elements: one of the allotropic forms of uranium (β -U) [3] and a metastable crystalline modification of tantalum (β -Ta) [4]. The σ phase is a brittle phase and is of some technological importance in connection with stainless steels. The interest in the σ phase goes far beyond its technological properties and is related to the fundamental problem of structure stability in crystal chemistry and physics of metals and alloys. Although the Fe–Cr alloy system has been the subject of some theoretical studies [5, 6], they were only concerned with the bcc structure.

The equiatomic FeCr alloy is isoelectronic to the manganese that crystallizes at ambient conditions in a complex cubic structure (α -Mn) with 58 atoms in the unit cell, space group $I\bar{4}3m$, lattice parameter $a = 8.911$ Å, Pearson symbol $cI 58$ [7]. It was shown by Fujihisa and Takemura [8] that the α -Mn structure is stable at high pressures up to 165 GPa where a new diffraction peak appeared, indicating a phase transition. One of the main factors of crystal structure stability

for such complex low-symmetry structures is the valence electron energy contribution to the total crystal energy that increases under compression [9]. Therefore structural high-pressure studies provide new data for an understanding of the formation and stability of the complex low-symmetry phases.

The aim of this paper is to study the structural behavior of the σ phase FeCr under high pressure. It is expected to observe the stability of the σ phase at high compression in similarity to the α -Mn, assuming the same mechanism of stability. The main factors of structural stability are discussed by analyzing the configuration of a large Brillouin–Jones zone and its filling with electron states [10].

2. Experimental details

An equiatomic FeCr alloy was prepared by melting of proper amounts of both Fe and Cr 4N purity in a levitation inductance furnace under Ar atmosphere. After cooling to room temperature, the alloy was cut with a spark cutting machine into sheets of ~ 0.2 mm thickness and annealed in vacuum at 700 °C for 100 h. The alloy composition was determined by x-ray microprobe analysis with resulting chemical content of 51 at.% Fe and 49 at.% Cr with a deviation up to 0.45 at.%. Structural analysis of the samples at ambient conditions was performed using a SIEMENS diffractometer and resulted in a tetragonal structure of the σ phase with lattice parameters close to the literature data [1].

High-pressure studies were performed in a diamond anvil cell with a culet of 300 μ m using a Re gasket and a ruby chip for pressure measurements. Experimental details are described in [11]. A piece of the sample was placed into the

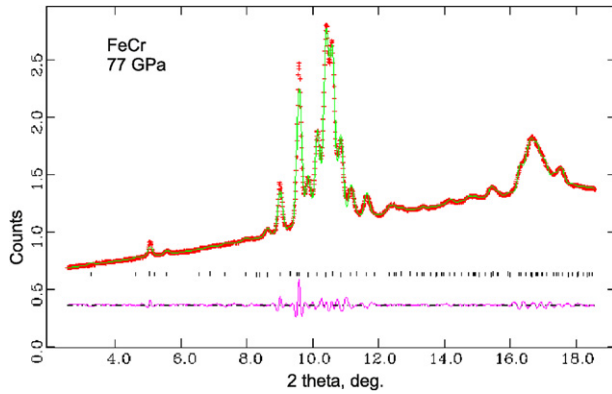


Figure 1. Diffraction pattern of the FeCr alloy at 77 GPa ($\lambda = 0.3344 \text{ \AA}$). Crosses (red) show experimental data; solid line (green) is the Rietveld refinement curve for the tetragonal σ -type structure with the lattice parameters $a = 8.2441(3) \text{ \AA}$, $c = 4.2552(2) \text{ \AA}$. Calculated peak positions are indicated by tick marks below the spectrum; the curve below the tick marks is the difference between the observed and calculated spectra. (This figure is in colour only in the electronic version)

gasket hole of $125 \mu\text{m}$ diameter and $30 \mu\text{m}$ thickness with the addition of the silicon oil as pressure transition medium. X-ray powder diffraction measurements were made with synchrotron radiation at IDD-13 of the Advanced Photon Source (Argonne National Lab). The diffraction data were analyzed with the Rietveld method using the FULLPROF program [12]. The volume compressibility data were fitted with the third-order Birch–Murnaghan equation of state [13].

3. Results and discussion

Collected x-ray diffraction patterns showed that the σ phase FeCr remained stable up to 77 GPa, the highest pressure reached in this study. The diffraction pattern of the FeCr alloy at 77 GPa is shown in figure 1. The Rietveld refinement on the basis of the tetragonal σ -type structure, space group $P4_2/mnm$, resulted in lattice parameters $a = 8.2441(3) \text{ \AA}$, $c = 4.2552(2) \text{ \AA}$, by assumption of the same atomic positions as at ambient pressure [1]. These values correspond to a cell volume compression of $V/V_0 = 0.817$.

Analysis of the pressure dependence of cell volume results in the equation of states given in figure 2 with the values of bulk modulus $K_0 = 217(5) \text{ GPa}$ and its pressure derivative $K'_0 = 5.8(2)$. It is interesting to compare the compressibility of the σ phase FeCr to that of the constituent elements. The bulk modulus K_0 for the bcc forms of Cr and Fe is 161 and 173 GPa for antiferromagnetic Cr and ferromagnetic Fe, respectively [14] and is lower than that of the σ phase. For the paramagnetic ε -Fe, the value of K_0 was found to be 163(8) GPa [15] which is still lower than that of the σ phase FeCr. Thus, the FeCr in its σ phase appears to be less compressible than the phases of the constituent elements. In contrast, the pure element Mn, isoelectronic to the FeCr alloy, has a much lower value of the bulk modulus, $K_0 = 158 \text{ GPa}$ [8].

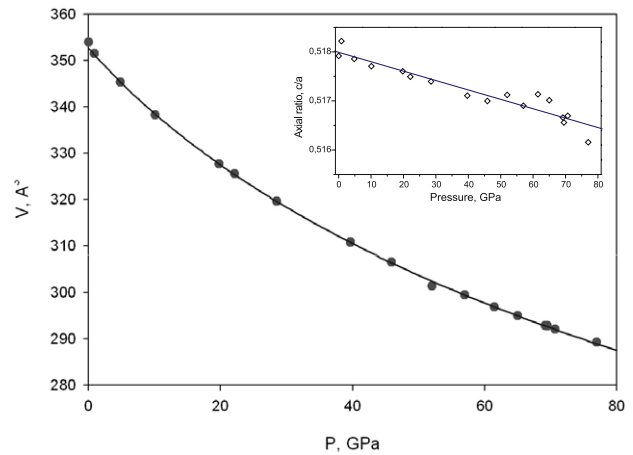


Figure 2. Variation of the cell volume for the σ phase in FeCr with pressure. Circles show experimental data (the experimental error is smaller than the symbol size); solid curve is the fit of the equation of states with $K_0 = 217(5) \text{ GPa}$ and $K'_0 = 5.8(2)$. The pressure dependence of the axial ratio c/a for the tetragonal cell is shown in the inset.

It should be noted that the tetragonal structure of the σ phase FeCr is compressed slightly anisotropically as can be concluded from the c/a behavior under pressure (see inset in figure 2). The compressibility along the c axis is somewhat higher than along the a axis; at pressure 77 GPa c/a decreases to 0.5161(1) from 0.5185(1) at ambient pressure.

In an attempt to analyze the factors of structural stability, we look at the configuration of Brillouin–Jones zones and the degree of their filling with electron states. To analyze the stability of such complex low-symmetry structures found in alloys, one can use the so-called large or extended Brillouin–Jones zones (further denoted as Brillouin zones) formed by planes corresponding to the strong reflections in the diffraction pattern [10]. When such a Brillouin zone lies close to a Fermi surface (considered as being close to a sphere), an energy pseudo-gap is formed and the valence electron energy is lowered, providing structural stability [16]. This mechanism of the structural stabilization has been known as the Hume-Rothery mechanism. The classical example of a complex phase stabilized by the Hume-Rothery mechanism is a γ -phase Cu_5Zn_8 (see figure 3(a)). The strong reflections of $\langle 330 \rangle$ and $\langle 411 \rangle$ type form in k space a polyhedron with 36 planes of nearly spherical form that is filled with electron states by $\sim 93\%$, assuming an average number of valence electrons per atom 1.61 [16]. A Brillouin zone formed by many planes that lie close to k_F and filled with electron states by approximately 90%—these are the main features for the Hume-Rothery mechanism for the stabilization of the complex low-symmetry structures. This mechanism has been shown to increase on compression, when the contribution of the electronic energy to the total structure energy increases [17]. Indeed, the γ -phase in Cu_5Zn_8 has been found stable to at least 50 GPa, illustrating the enhancement of the Hume-Rothery mechanism under pressure [18].

Now we apply similar considerations to the σ phase in FeCr. In the first paper where the structure of the σ phase was solved [1] two ‘prominent’ Brillouin zones have been

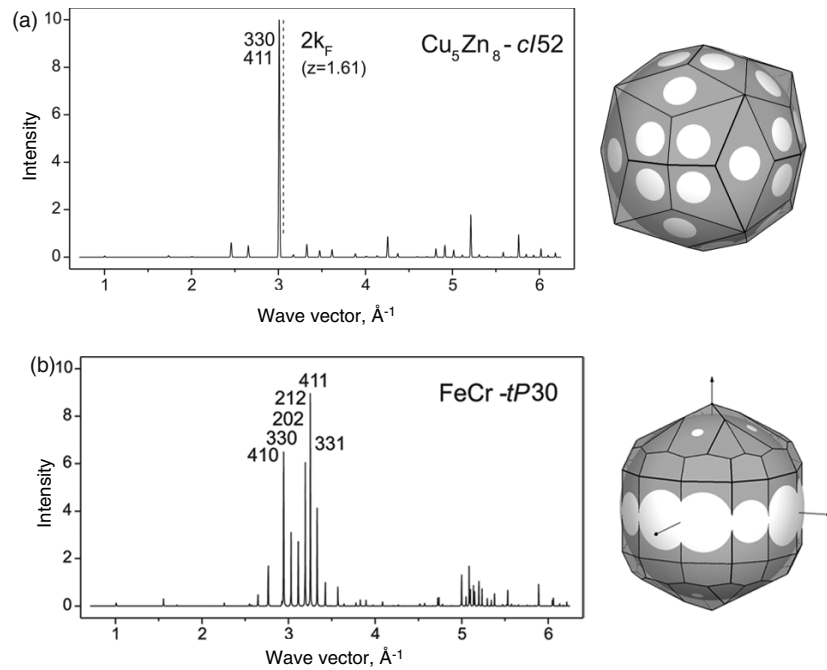


Figure 3. Diffraction patterns (calculated) (left) and corresponding Brillouin–Jones zones with the inscribed Fermi sphere (right) for phases Cu_5Zn_8 (a) and FeCr (b). The planes chosen for the BZ construction are indicated with their hkl indices. The position of $2k_F$ for Cu_5Zn_8 (dashed line) corresponds to $z = 1.61$ electrons/atom. Estimation of k_F for FeCr from the number of electron states in the Brillouin–Jones zone with a degree of filling of about 90–93% as for Cu_5Zn_8 results in $2k_F \approx 3.1 \text{ \AA}^{-1}$ for $z \approx 1.5$ (see the text).

considered which are related to two groups of diffraction peaks with relatively large structure factors clustered around wave vectors ~ 3.1 and $\sim 5.1 \text{ \AA}^{-1}$ (see figure 3(b)). The second strong Brillouin zone is assumed in [1] to be responsible for phase stability, containing ~ 7 electrons per atom. However, we consider the first ‘prominent’ polyhedron to be important for the structure stability that shows a high degree of sphericity and is bounded by 60 planes (figure 3(b)). Although, the Fermi surface of FeCr is more complex than a sphere, the present simple approach allows us to analyze the degree of filling by electron states of the Brillouin zone that we suggest is responsible for structural stability. Indeed, the first ‘prominent’ Brillouin zone lies close to a sphere with a radius k corresponding to a position of $2k \sim 3.1 \text{ \AA}^{-1}$, as shown in figure 3(b) and this zone accommodates ~ 1.65 electrons per atom. Zone filling by 90–93% as for other Hume-Rothery phases, corresponds to ~ 1.5 electrons per atom. Thus, we have shown that the existence of the nearly spherical Brillouin–Jones zone containing around 1.5 electron states per atom could be an important factor for the stability of the σ phase, in analogy with Hume-Rothery phases known for other alloys. The structural stability of the σ phase up to 77 GPa supports the suggestion that the lowering of the electronic energy is one of the main factors responsible for the formation and stability of this phase.

It should be noted that selection of the extended Brillouin–Jones zone for the σ phase (figure 3(b)) is related to the zone selection for the isoelectronic element Mn in its α -structure. The space group of α -Mn is the same as for the γ -phase, $I\bar{4}3m$, and diffraction patterns of both phases are similar with one strong diffraction peak that gives a similar Brillouin zone as

for the γ -phase Cu_5Zn_8 (figure 3(a)). The only difference is that the number of electrons per atom corresponds to ~ 1.45 for α -Mn instead of 1.61 for γ -phase Cu_5Zn_8 that relates to the number of atoms in the unit cell, 58 and 52, respectively. Within the approach of analyzing the BZ configuration and the degree of filling by electronic states, only the sp-electrons are considered as ‘structure controlled electrons’ [19]. Formation and high-pressure stability of transition metal alloy phases can have common ground with the structural stability in binary alloy systems of simple metals based on the Hume-Rothery mechanism, as illustrated for the simple metal alloy system of Li–Be in [20]. Recent studies on binary compounds Fe_5Si_3 and Ni_2Si revealed the stability of their structure up to 75 GPa [21]. The fact that the binary phases in these systems remained stable to high pressures makes these results similar to the present study and analogous considerations of the Brillouin–Jones zones could be applied.

In conclusion, the structural stability of the complex, low-symmetry phase in FeCr was observed in the pressure range up to 77 GPa. This observation provides evidence for the importance of the electronic energy contribution to the total energy and the increase of this factor on compression. The stability of the σ phase can be related to the Hume-Rothery effect based on the configuration of the large Brillouin–Jones zone. The results on Fe-alloys under pressure will provide experimental grounds for theoretical considerations.

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