On the Spinodal Decomposition of Wolframite

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Investigations by transmission electronmicroscopy (TEM) of hydrothermally treated wolframites at 200 °C and 1 kbar exhibit in contrast to untreated samples spinodal decomposition. The scales of modulation for those wolframites are given ($\lambda = 65 - 250$ Å). Alongside TEM-investigations, diffraction patterns were determined.

Introduction

Many crystallophysical investigations have shown that within the mixed crystal series wolframite deviations in the degree of homogeneity occur (Young and Millman [1]; Maksimyuk and Chernyshev [2]; Weitzel [3]). As other authors using the electron microprobe have shown, no singularly definable mixed crystal composition exists in most wolframites. In general more or less heterogeneously intergrown mixed crystals of variable composition, even into the micro region, are encountered (Moore and Howie [4]; Willgallis [5]). In the course of their electronmicroscopic investigations Maksimyuk et al. [6] discovered one natural sample (locality: Zagan-Dava, Mongolia) which exhibits the lamellar microstructure characteristic of spinodal decomposition. Further examples of this could however not then be found.

Considering the results of the investigations here described, limited miscibility at low temperatures appears very probable from the course taken by the progressive decomposition of wolframite mixed crystals. Unmixing can be the result of two different processes, i.e. by nucleation or by spinodal decomposition. The critical temperature for both processes must lie below 300 °C, as unlimited miscibility up to this temperature was demonstrated for the system $FeWO_4$–$MnWO_4$ experimentally [7]. Because of the small differences between the lattice parameters, the system hübnerite–ferberite exhibits favourable conditions for spinodal decomposition. Since the difference of the lattice parameters determines the orientation of the fluctuations in composition and as a_0 shows the largest difference between hübnerite and ferberite, Maksimyuk et al. [6] expect $\langle 100 \rangle$ as the direction of spinodal decomposition of wolframite.

As an alternative to the classical nucleation mechanism, that of spinodal decomposition of homogeneous mixed crystals can be accorded equal ranking (Cahn [8]). In this paper a systematic investigations by electronmicroscope of the spinodal decomposition of natural wolframites following hydrothermal treatment in contrast to untreated samples is reported. Alongside transmission electronmicroscope investigations (TEM), diffraction patterns were determined.

Experimental procedure

10 samples of wolframite from 10 different deposits were investigated. Their composition had been established previously (Willgallis [5]) and reported after Groves and Baker [9] according to the ratio:

$$\frac{\mathrm{MnO}}{\mathrm{FeO} + \mathrm{MnO}} \times 100 = [\mathrm{Mn}] .$$

The average composition ($\bar{x}$) of the samples, some of which were very heterogeneous, was obtained as [$\overline{\mathrm{Mn}}$] from a maximum of 45 point analyses. The variation coefficient of [$\overline{\mathrm{Mn}}$] was reported in relative % as the ratio of the standard deviation (s) and the average ($\bar{x}$), i.e.:

$$Vc = \frac{s \cdot 100}{\bar{x}} \text{ rel.\%} \quad \text{(Willgallis [5])} .$$

Finely powdered material of the original samples, as well as similar material which had been subjected to hydrothermal heat treatment were investigated by transmission electronmicroscopy, using a "Siemens E M 1139" at 80 kV. Hydrothermal treatment was carried out for 70 or 140 hours respectively at a temperature of 200 °C and a pressure of 1 kbar in H_2O-filled quartz ampoules in autoclaves

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made by Tempress, type MRA 112 A. The temperature chosen (200 °C) is 100 °C below the temperature at which complete miscibility still obtains in the system $FeWO_4$–$MnWO_4$. Lower temperatures were not utilized since it was assumed that the rate of diffusion of the bi-valent metal cations would rapidly diminish. On all samples not only TEM was carried out, but electron diffraction patterns were also determined.

Results

The composition of the samples and the parameters pertaining to the hydrothermal treatment are summarized in Table 1. As can be seen, none of the untreated samples showed spinodal decomposition, whereas after treatment samples from 4 different localities exhibited the typical lamellar decomposition textures. The composition of these wolframites lies between the values 15–27 for [$\overline{Mn}$]. For samples with [$\overline{Mn}$]-values below 13, as well as for those between 54 and 63 spinodal unmixing could not be detected after either 70 or 140 hours of hydrothermal treatment. Figure 1 shows spinodal decomposition of a sample (DDR 8) after treatment duration of 140 hours using transmission electron microscopy. The diffraction patterns of spinodally decomposed wolframites exhibit "satellite reflexes". The existence of this type of dispersion can be regarded as further confirmation of spinodal decomposition (Jantzen, Herman [10]). In Fig. 1 a satellite reflection accompanying the diffraction pattern of the spinodally decomposed sample DDR 8 is included. In Table 1 the scales of modulation for those wol-

Table 1. Provenance, composition and treatment parameters of wolframites (hydrothermal treatment: 200 °C, pressure: 1 kbar).

Sample	Locality	[$\overline{Mn}$] ±	*Vc*	Treatment duration (hours)	Spinodal decomposition		λ (Å)
					observed	not observed	
BO 2	Chojlla Bolivia	8	23	untreated 70 140		+ + +	
P 1	Panasqueira Portugal	13	2	untreated 70 140		+ + +	
P 9	Sabrozal Vila Real Portugal	15	93	untreated 70 140	 + +	+ 	 65 125
DDR 8	Neudorf Harz DDR	20	9	untreated 70 140	 + +	+ 	 85 125
RSR 2	Essex Vale Rhodesia	24	26	untreated 70 140	 + +	+ 	 125 170
DDR 10	Tirpersdorf Oelsnitz DDR	27	86	untreated 70 140	 + +	+ 	 100 250
GB 2	Kit Hill Cornwall UK	54	22	untreated 70 140		+ + +	
RC 1	West- kuangtung PR of China	58	5	untreated 70 140		+ + +	
CS 5	Sadisdorf Bohemia CSSR	62	3	untreated 70 140		+ + +	
DDR 1	Zinnwald DDR	63	9	untreated 70 140		+ + +	

Fig. 1. Transmission electron micrograph of a hydrothermally treated wolframite (DDR 8) at 200 °C and 1 kbar for 140 hours (with an enlargement of a diffraction spot which shows satellites).

framites that show decomposition as determined by transmission electron microscopy are given. They are denoted as "wavelength λ" after Daniel and Lipson [11]. It can be seen that the heterogeneous sample DDR 10 ($Vc \pm 86$) shows a higher value of λ compared with more homogeneous wolframites after treatment for 140 hours. In contrast the sample DDR 8 ($Vc \pm 9$) under equal conditions only yields a value of $\lambda = 125$ Å. Sample RSR 2 after only 70 hours attains a value for λ which was only observed in samples P 9 and DDR 8 after 140 hours. Sample DDR 10 with $\lambda = 100$ Å also yields a slightly lower value after 70 hours treatment when compared with RSR 2. This might be regarded as evidence of the influence of imperfections, which vary from sample to sample, on the kinetics of spinodal decomposition. Since an increase in the number of imperfections is to be expected when comparing pegmatitic and hydrothermal wolframites, it is possible that low temperature phases can be unmixed after shorter treatment for spinodal decomposition.

Conclusions

From the occurrence of spinodal decomposition in wolframites the existence of points of inflexion on the curve relating the free enthalpy of mixing ΔG_m with the composition of the system $FeWO_4$–$MnWO_4$ can be inferred. The course taken can be that expected of systems with partial miscibility and a miscibility gap at low temperatures (Fast [12]). In the region between the points of inflexion minute fluctuations in composition lead to a reduction in the free enthalpy of mixing and thereby initiate spinodal decomposition (Cahn [8]).

Proof of the existence of spinodal decomposition textures in minerals is of interest in the first instance for petrological problems. Above all it is important since the lamellar width (λ) might be used as thermogenetic indicator for the determination of the duration of periods of cooling or the registration of secondary thermal effects.

The fact that no evidence of spinodal decomposition could be found in the untreated samples would tend to indicate prolonged periods of cooling in nature as well as appreciable velocities of diffusion of the bi-valent cations in the wolframite lattice at temperatures below 200 °C.

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