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Letter

A revision of the central part of the Cr–Ge phase diagram

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ABSTRACT

The central part of the Cr–Ge phase diagram was re-investigated using powder-X-ray diffraction (XRD), differential thermal analysis (DTA) and chemical vapour transport (CVT). It was found that the phase Cr_5Ge_3 (Si_3W_5-type structure) does not show a polymorphic transformation as reported previously, but rather undergoes a eutectoidic decomposition reaction $Cr_5Ge_3 = Cr_3Ge + Cr_{11}Ge_8$ at $T = 996\,^\circ C$. A revised version of the corresponding region of the phase diagram is given.

1. Introduction

A detailed review of the binary Cr–Ge system was given by Gokhale and Abbaschian [1]. This assessed phase diagram is based on experimental data from the sixties by Zagryazhskii et al. [2] and Kalishevich et al. [3], the seventies by Rawal and Gupta [4] and Kawasumi [5] and the beginning eighties by Godat and Feschotte [6], whereat the latter work is considered to be the most reliable.

Five stable intermetallic phases were reported: Cr_3Ge, Cr_5Ge_3, $Cr_{11}Ge_8$, CrGe and $Cr_{11}Ge_{19}$, which all form in peritectic reactions. A broader homogeneity range was only observed for Cr_3Ge. The crystal structure of Cr_5Ge_3 was originally investigated by Zagryazhskii et al. [2] and it was found to adopt the Si_3W_5-type structure (Pearson symbol *tI*32, space group *I*4/*mcm*). The authors synthesised the compound at 1200 °C. Later, Godat and Feschotte [6] reported a polymorphic transformation of Cr_5Ge_3 at 1002 °C based on DTA-data. They assigned the tetragonal Si_3W_5-type structure as low temperature modification, but they did not give any information on the crystal structure of the proposed high temperature phase.

Recently, Li et al. [7] gave a thermodynamic assessment of the Cr–Ge system by using the CALPHAD technique. The data from Gokhale and Abbaschian [1] were well reproduced in this assessment. Neddermann et al. [8] performed chemical vapour transport experiments in the system Cr–Ge in a temperature gradient from 780 °C to 880 °C using I_2 as transport agent. It was shown that all phases that appear in the phase diagram can be obtained by CVT. The transport of Cr_3Ge was assessed to be congruent while the other phases are transported incongruently.

In the course of several CVT-experiments we performed in the system Cr–Ge, we observed results in conflict to the current version of the Cr–Ge phase diagram. Thus we decided to perform a systematic study of the phase equilibria involving Cr_5Ge_3 using annealed bulk samples. The corresponding results are presented here.

2. Experimental

As starting materials for all alloys germanium lump (6 mm, Alfa Products, m6N+), chromium pellets (Johnson Matthey, 99.999%) and chromium lump (Aviquipo-Corp, 99.997%) were used. The proper amounts of the weighted elements were mixed and arc-melted three times on a water-cooled copper plate under inert argon atmosphere. Zirconium was used as a getter material. Samples were subsequently sealed in evacuated quartz-glass ampoules and were annealed at different temperatures.

The CVT-experiment was carried out in an evacuated quartz-glass tube with a length of 12 cm, an outer diameter of 20 mm and a wall thickness of 1.8 mm. As transport agent served iodine. A two-zone-furnace was used to create the temperature gradient from 780 °C to 880 °C. The chemical vapour transport lasted for 48 h.

All samples, including source and sink of the CVT-experiment, were investigated by powder-X-ray diffraction using a Bruker D8 diffractometer with Cu-Kα radiation in Bragg-Brentano reflecting geometry. DTA experiments were performed on a Netzsch-DTA 404S employing alumina- as well as quartz-glass crucibles at 5 K/min using Pt/PtRh thermocouples for temperature measurements.

Sample compositions, heat treatments and XRD results are summarized in Table 1.

3. Results and discussion

In our CVT-experiment we used sample 1 (see Table 1) as source, which contained the two phases Cr_3Ge and Cr_5Ge_3. According to Neddermann et al. [8] a sink composition of Cr_5Ge_3 plus $Cr_{11}Ge_8$ was to be expected in this experiment, but in contradiction to expectations, we did not find Cr_5Ge_3 after the transport. Instead we obtained $Cr_{11}Ge_8$ in equilibrium with Cr_3Ge in the sink. In addition we observed that also the remaining source was completely converted to $Cr_{11}Ge_8 + Cr_3Ge$ after the experiment; i.e. Cr_5Ge_3 was not longer found in the powder pattern.

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Table 1
Sample compositions, heat treatments and phase compositions determined by XRD.

Sample No.	Nominal composition at% Cr / at% Ge	Annealing procedure	Phases detected by XRD
1	70/30	As cast	$Cr_3Ge + Cr_5Ge_3$
		880 °C/CVT sink, 48 h	$Cr_{11}Ge_8 + Cr_3Ge$
		780 °C/CVT source, 48 h	$Cr_3Ge + Cr_{11}Ge_8$
2	60/40	1000 °C/20 days	$Cr_5Ge_3 + Cr_{11}Ge_8$
3	65/35	1000 °C/20 days	$Cr_3Ge + Cr_5Ge_3$
		After DTA	$Cr_3Ge + Cr_5Ge_3$
4	62/38	800 °C/31 days	$Cr_3Ge + Cr_{11}Ge_8$
		After DTA	$Cr_5Ge_3 + Cr_3Ge$

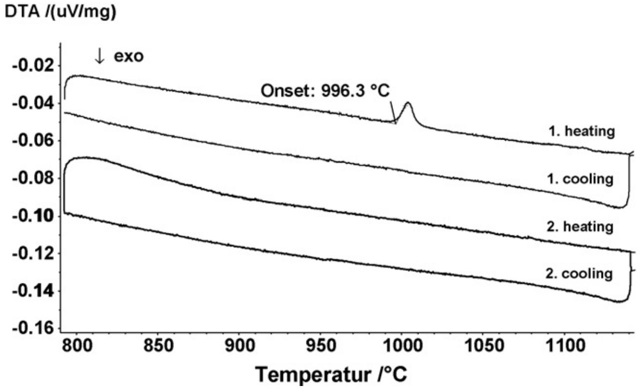

Fig. 1. DTA curves observed for sample 4. Two heating- and cooling cycles at 5 K/min are shown.

These results raised some doubts regarding the stability of Cr_5Ge_3 in the temperature range of our experiment (between 780 °C and 880 °C). So we decided to perform some additional experiments on bulk samples in order to test the phase equilibria around Cr_5Ge_3 at different temperatures. Two samples were prepared at the chromium rich and chromium poor side of the Cr_5Ge_3 phase and annealed at 1000 °C. One sample was prepared directly at the composition of Cr_5Ge_3 and annealed at 800 °C. The results of X-ray powder diffraction after annealing are listed in Table 1. It was found that Cr_5Ge_3 is not stable at 800 °C, but exists as stable modification at 1000 °C. This fact points to a eutectoidic decomposition of Cr_5Ge_3 at some temperature between 800 °C and 1000 °C.

DTA experiments were performed with the samples 3 and 4 in order to determine the reaction temperature. The samples were cycled two times between 800 °C and 1150 °C. The DTA curves of sample 4 annealed at 800 °C are shown in Fig. 1. A clear endothermic thermal effect at 996 °C was observed on first heating, which is obviously connected to the formation of Cr_5Ge_3. Equilibrium was not re-established on cooling, so the corresponding effect was not found in subsequent heating- and cooling segments (Fig. 1). Correspondingly the sample contained Cr_5Ge_3 instead of $Cr_{11}Ge_8$ after the DTA experiment (Table 1). For sample 3 annealed at 1000 °C which already contained Cr_5Ge_3 in equilibrium with Cr_3Ge we did not find any effect and the original phase composition was preserved after the experiment. Thus, the eutectoidic transformation can be well detected on heating of equilibrated samples, but it is too slow to occur on cooling with 5 K/min and extended heat treat-

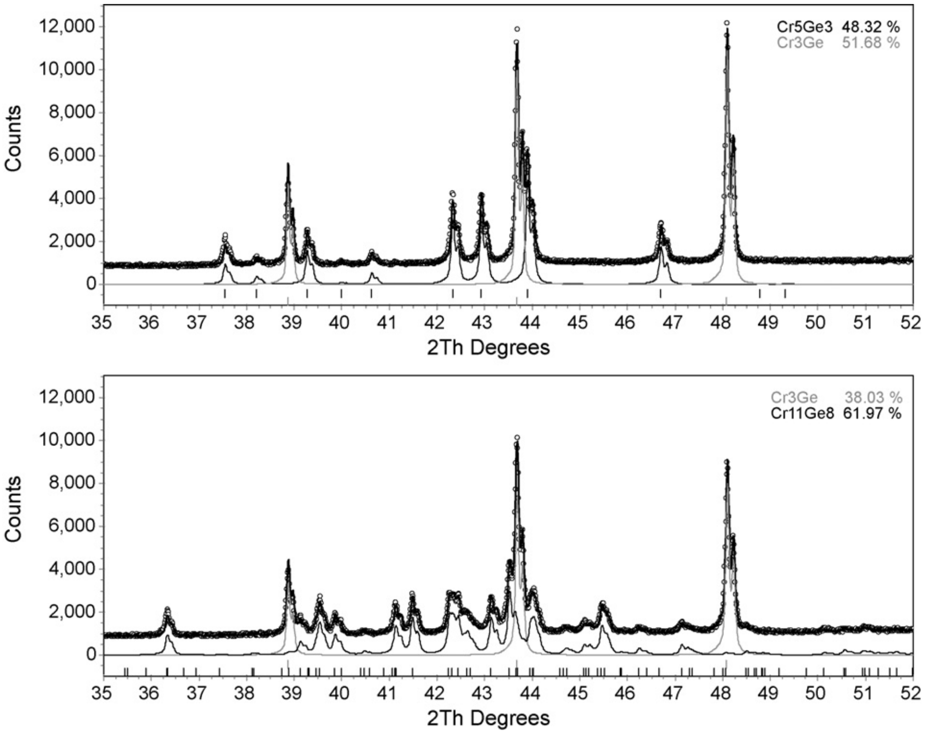

Fig. 2. Detail of the refined powder patterns of sample 3 (up) and sample 4 (down) annealed at 1000 °C and 800 °C, respectively. Circles: experimental intensities; black line: calculated pattern; bottom inserts show the calculated diffraction lines of the respective phases.

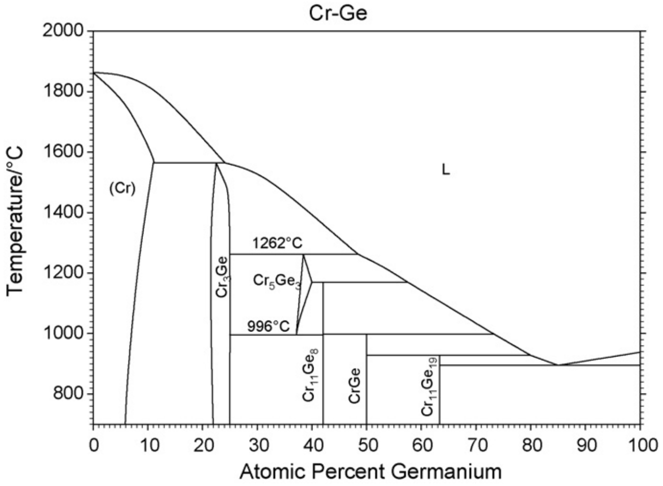

Fig. 3. The revised Cr–Ge phase diagram according to the current work.

ment below the reaction temperature is needed to establish the low temperature equilibrium [$Cr_3Ge + Cr_{11}Ge_8$].

It should be noted that the thermal effect observed here is nearly identical to that obtained by Godat and Feschotte [6] (1002 °C), who attributed this effect to a polymorphic transformation of Cr_5Ge_3. However, there is no experimental evidence that another modification of Cr_5Ge_3 exists. Neither the annealed nor the as-cast samples did show any additional diffraction lines that could be attributed to a second modification of Cr_5Ge_3. The diffraction patterns observed of samples 3 and 4 after Rietveld refinement are shown in Fig. 2.

In summary, our results maybe interpreted as follows: The phase Cr_5Ge_3 does not undergo a polymorphic transformation as reported earlier [6] and it crystallises only in the Si_3W_5 type. This phase is only stable at elevated temperatures; it is formed in a peritectic reaction at 1262 °C and decomposes eutectoidically at 996 °C. Below this temperature Cr_3Ge is in equilibrium with $Cr_{11}Ge_8$. The revised phase diagram of Cr–Ge according to our results is shown in Fig. 3.

References

[1] A.B. Gokhale, G.J. Abbaschian, Bull. Alloy Phase Diagram 7 (1986) 477.
[2] V.L. Zagryashskii, A.K. Shol'ts, P.V. Gel'd et, N.V. Kuźmenko, Sov. Powder Metall. Met. Ceram. 44 (1966) 639.
[3] G.I. Kalishevich, V.I. Zagryazhskii, L.V. Shchipanova, N.N. Serebrennikov, P.V. Gel'd, Russ. J. Phys. Chem. 43 (1969) 132.
[4] B. Rawal, K.P. Gupta, J. Less-Common Met. 27 (1972) 65.
[5] I. Kawasumi, S. Konishi, M. Kubota, M. Sakata, Jpn. J. Appl. Phys. 17 (1978) 2173.
[6] D. Godat, P. Feschotte, J. Less-Common Met. 72 (1980) 99.
[7] M. Li, C. Guo, C. Li, Z. Du, J. Alloys Compd. 481 (2009) 283.
[8] R. Neddermann, R. Wartchow, M. Binnewies, Z. Anorg. Allg. Chem. 624 (1998) 733.