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Phase transformation of the compound V_3Ga induced by mechanical grinding

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Abstract. The A15 intermetallic compound V_3Ga was subjected to grinding in a high-energy ball mill. X-ray diffraction showed that the material transformed from the A15 phase to the high-temperature BCC solid solution after 40 hours of grinding. This state did not change upon further milling. Differential scanning calorimetry revealed two exothermic peaks with a total heat content of 3.0 kJ mol^{-1} . After the heating the material again exhibited the A15 structure. The activation energy of the first peak turned out to be the same as the activation energy for reordering of thermally disordered V_3Ga . The results were interpreted in terms of atomic disordering.

1. Introduction

Intermetallic compounds may transform to the amorphous state, when they are subjected to mechanical grinding in a high-energy ball mill. The first indications for such a reaction were found by Yermakov *et al* [1] in the Y–Co system. A number of years later such transformations were also observed in the Ni–Ti [2] and Ni–Zr [3] systems, and since then the number of intermetallic compounds that were found to exhibit this amorphization reaction has been increasing. In contrast to the amorphization caused by mechanical alloying of the pure components, where there is a gain in free energy due to the mixing of the elements, amorphization caused by mechanical grinding leads to a higher energy level of the system. An interesting question is that of in which form energy can be stored in the material during grinding. In principle there are three possibilities, namely in the form of chemical disorder, point and line defects, and grain boundaries. Most theoretical work speculates that atomic disorder is the main source of energy storage [4–6]. Experimentally, disorder during the early stage of ball milling was really detected in $NiTi_2$ by differential scanning calorimetric (DSC) [7], in Ni_3Al by x-ray examination [8], in Nb_3Sn by following the degradation of the superconducting transition temperature [9] and in $CoGa$ by measuring magnetic properties [10]. In contrast to the other compounds, $CoGa$ turned out not to transform to the amorphous state even after long periods of milling.

In order to obtain more insight into in which form energy is stored in an intermetallic compound, we decided to investigate the A15 compound V_3Ga . This compound is known to exhibit some anti-site disorder at higher temperatures [11]. Moreover the A15 phase exists up to a temperature of about 1300°C , above which the material transforms

to a disordered solid solution of gallium in BCC vanadium. Therefore it is to be expected that the introduction of atomic disorder in V_3Ga by grinding may transform the compound into the BCC phase. After such a transition the compound is certainly not able to store more energy in the form of atomic disorder, for the simple reason that the BCC phase is a disordered one. *A priori* there is no reason for this phase not to increase its energy due to crystallite refinement or formation of lattice defects upon further milling. Therefore, if atomic disorder is the cause of the crystalline-to-amorphous transformation, this BCC phase would certainly not amorphize. In the present paper we show that this prediction is correct.

2. Experimental procedure

The intermetallic compound V_3Ga alloy was obtained by arc melting of weighted amounts of pure vanadium and gallium in a purified argon atmosphere. The arc-melted button was crushed into small pieces. To remove mechanical stresses and for homogenization the specimen was annealed at 1000 °C for five days. Thermodynamic equilibrium was established at 600 °C by annealing at this temperature for four weeks. The ball milling was carried out in a hardened steel vacuum vial (inner diameter 6.5 cm) with a tungsten carbide bottom. Inside the vial, a hardened steel ball with a diameter of 6 cm was kept in motion by a vibrating frame (Fritsch: Pulverisette 0), upon which the vial was mounted. To prevent reactions with oxygen or nitrogen, the milling was performed under continuous pumping. During the milling the vacuum was kept at a level of about 10^{-6} Torr. The starting amount of material was 2 g, which was milled for 40 h. During this process the milling was stopped at 20 h and 30 h to take an x-ray diffractogram and after the x-ray measurement the powder was used for further milling. X-ray diffraction patterns were taken at room temperature by means of a Philips vertical powder diffractometer using $Cu K\alpha$ radiation. For an accurate measurement of the lattice parameter the sample was mixed with silicon powder as a standard. A high-temperature film scan was made by using a Guinier-Lénné camera, while the heating rate was $10 K h^{-1}$. For this high-temperature scan the powder was compacted by applying a pressure of 2 ton and mounted in a PtRh sample holder. To avoid oxidation the scan was carried out in a helium atmosphere. The DSC measurements were carried out on the Setaram DSCIII at the Department of Chemistry of the University of Amsterdam. The DSC measurements were performed in an argon flux to protect the sample against oxidation. The heating rates of DSC were varied between 1 and $10 K min^{-1}$. The compositional analyses were performed on a Jeol JSM 840 A scanning electron microscope at the Technical University of Eindhoven.

3. Results

Compositional analysis of the starting material yielded a composition of 70 at.% V and 30 at.% Ga. The peaks in the x-ray diffractogram (bottom curve of figure 1) can all be identified as A15 peaks, showing that the sample is single phase as was to be expected for this composition on the basis of the phase diagram [12]. The lattice parameter is $4.8270 \pm 0.0007 \text{ \AA}$, not far from the value of 4.825 \AA from [12] for the same composition.

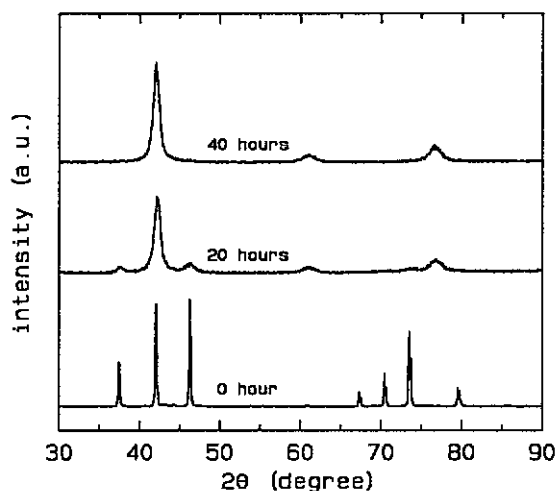


Figure 1. X-ray diffraction patterns of V_3Ga after various milling periods.

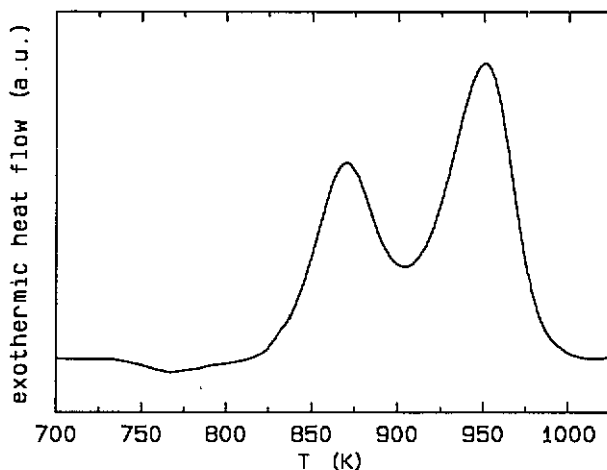


Figure 2. A DSC scan with a heating rate of 10 K min^{-1} for the sample ball milled for 40 h.

Figure 1 shows also the x-ray diffraction patterns for the samples ball milled for periods of 20 and 40 h. It is observed that for 20 h of milling the intensity of the A15 peaks decreases and that some new peaks appear. After 40 h of milling the A15 peaks have disappeared and the x-ray pattern is characteristic of a BCC structure. Apparently the sample was completely transformed in the BCC V–Ga solid solution that is found in the equilibrium phase diagram at high temperature. The lattice parameter of this phase was determined as $3.0465 \pm 0.0033\text{ \AA}$, within experimental error not far from 3.051 \AA as obtained by [12] after quenching the BCC phase from the temperatures above the phase transition. The sample milled for 40 h contained 1 at. % of iron, which came from the milling tools.

A scan by a differential scanning calorimeter of a sample milled for 40 h is shown in figure 2. The heating rate was 10 K min^{-1} , the temperature range 300–1050 K. Two

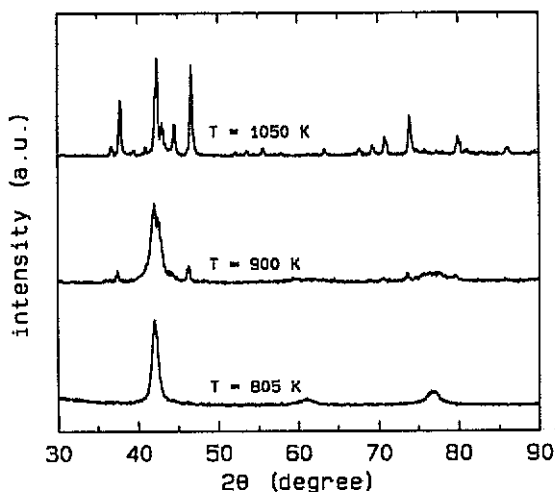


Figure 3. X-ray diffraction patterns for samples after heating to different temperatures in DSC.

exothermic peaks are observed at 869 K and 950 K, respectively. Before the first exothermic peak starts, a small endothermic peak is detected. The total heat evolved during the transition is 3.0 kJ mol^{-1} , 40% in the first peak, 60% in the second peak. In further experiments milled samples were heated in the DSC to different temperatures and immediately cooled down. Results of the corresponding x-ray diffraction patterns are presented in figure 3. The bottom curve is the result for a sample heated to 805 K, i.e. the temperature above which the first peak starts. The pattern is clearly still a BCC pattern. The second diffractogram represents a sample heated to 900 K, just between the two peaks. This pattern shows a mixture of BCC and A15 structures. The top curve reveals the results for a sample heated to 1050 K, the temperature above the second peak. The pattern is mainly A15 with a few small additional peaks, which could not be identified. The BCC peaks have completely disappeared. This transition from the BCC structure to the A15 structure is corroborated by a Guinier-Lénné camera high-temperature film scan with the temperature range from room temperature to 1073 K for the same sample.

A series of heating rates, 1, 2, 5, 10 K min^{-1} , were applied to measure the dependence of the peak temperatures in DSC on heating rate for the milled sample. Kissinger [13] plots are displayed in figure 4 for both peaks. From the slopes of the straight lines the activation energies were calculated as 216 kJ mol^{-1} for the first peak and 297 kJ mol^{-1} for the second peak.

Upon further milling the sample remained in the BCC structure and did not amorphize.

Preliminary investigations on the 75 at.% V–25 at.% Ga compound showed very similar results.

4. Discussion

Inspection of the V–Ga equilibrium phase diagram [12] reveals a wide homogeneity range of the A15 V_3Ga compound. At high temperature this phase transforms to the

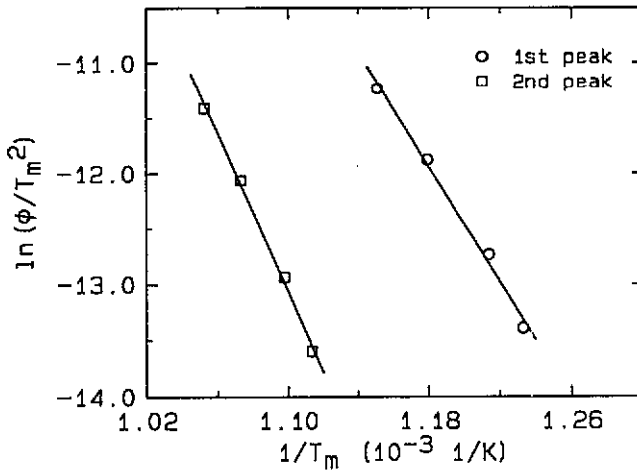


Figure 4. Kissinger plots corresponding to the two peaks in the DSC scan.

solid solution of gallium in BCC vanadium. The x-ray analysis of the starting material and of ball-milled samples shows that this phase transition is also generated by mechanical grinding (figure 1). Our results indicate clearly that by ball milling this metastable high-temperature phase is generated after 40 h. The iron impurity level (1 at.%) is low enough to exclude influence on the process. In [12] the BCC lattice parameter is given as a function of composition for samples with the BCC structure quenched from high temperatures. The lattice parameter for the ball-milled material is, within experimental error, close to the one interpolated from [12] for the composition of 70 at.% Vanadium. Heating of the metastable BCC sample in DSC reveals two peaks. After the first peak the sample is still partly BCC, after the second peak all BCC diffraction lines in the x-ray analysis have disappeared and A15 lines are predominant. Thus the metastable BCC solid solution transforms to the equilibrium A15 phase at temperatures, where the atomic mobility is high enough for establishing equilibrium. This is corroborated by a Guinier-Lénné camera high-temperature film scan. The precise nature of the two exothermic peaks in DSC is not completely clear. It is interesting to compare the activation energy, obtained from a Kissinger plot with the known reordering activation energy for V_3Ga thermally disordered by quenching as measured by Van Winkel *et al* [11]. In this investigation samples with 75 at.% V were quenched from high temperature in order to generate a small amount of thermal disorder. Annealing experiments at intermediate temperature, in which the reordering was followed as a function of time by following the restoration of the superconducting temperature, yielded a diffusion activation energy for the reordering process of 214 kJ mol^{-1} . This is almost the same as the activation energy obtained from the Kissinger plot of the process corresponding to the first peak in DSC. This makes it probable that the first peak is related to atomic movements during an ordering process.

Some of our results are rather similar to those by Oehring and Bormann [14]. They studied the A15 compound Nb_3Al and they also found an A15-to-BCC transition. A difference is that in V_3Ga the BCC phase at the composition studied exists in the equilibrium phase diagram at higher temperature, whereas in Nb_3Al it does not. Oehring and Bormann concluded that the main amount of free energy stored in their sample is stored in the form of chemical disorder.

We want to emphasize that after generating a disordered alloy by mechanical attrition, it is clear that no more energy can be stored in the material by disordering. The fact that V_3Ga transforms to a disordered BCC solid solution but not from this state further to an amorphous state indicates that energy stored in lattice defects or grain boundaries cannot drive the system to the amorphous state. In other words, if the disordered solid solution has a lower energy than the amorphous state, the material will not amorphize. This is completely in agreement with theoretical predictions [4–6, 15].

5. Conclusions

The A15 compound V_3Ga transforms to a BCC structure, when it is subjected to mechanical grinding in a high-energy ball mill. This state is a disordered solid solution of Ga in V; it exists in the equilibrium phase diagram at higher temperatures. Appropriate annealing procedures restore the A15 structure. The DSC measurements of this process reveal two exothermic transition peaks with a total heat content of 3.0 kJ mol^{-1} . The corresponding activation energies are 216 kJ mol^{-1} and 297 kJ mol^{-1} , respectively. The value of the first activation energy corresponds to the value measured in thermally disordered V_3Ga for the reordering process. Apparently the disordered state has a lower energy than the amorphous state. Clearly no more energy can be stored in the solid solution by disordering and this explains why the material does not amorphize upon further grinding.

Acknowledgments

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References

- [1] Yermakov A Y, Yurchikov Y Y and Barinov V A 1981 *Phys. Met. Metalloved.* **52** 50
- [2] Schwarz R B and Koch C C 1986 *Appl. Phys. Lett.* **49** 146
- [3] Weeber A W, Bakker H and de Boer F R 1986 *Europhys. Lett.* **2** 445
- [4] Johnson W L 1986 *Prog. Mater. Sci.* **30** 81
- [5] Massobrio C, Pontikis V and Martin G 1989 *Phys. Rev. Lett.* **62** 1142
- [6] Beke D L, Bakker H and Loeff P I 1990 *J. Physique Coll.* **14** C4 63
- [7] Schwarz R B and Petrich R R 1988 *J. Less-Common Met.* **140** 171
- [8] Koch C C, Janh J S C and Lee P Y 1989 *New Materials by Mechanical Alloying Techniques* ed E Arzt and L Schultz (Oberursel, Federal Republic of Germany): DGM Informationsgesellschaft p 101
- [9] Di L M, Loeff P I and Bakker H 1991 *J. Less-Common Met.* **168** 183
- [10] Di L M, Loeff P I and Bakker H 1991 *Proc. 7th Int. Conf. on Rapidly Quenched Materials; Mater. Sci. Eng. A* at press
- [11] van Winkel A and Bakker H 1985 *J. Phys. F: Met. Phys.* **15** 1565
- [12] van Vucht J H N, Bruning H A C M, Donkersloot H C and Gomes de Mesquita A H 1964 *Philips Res. Rep.* **19** 407
- [13] Kissinger H E 1957 *Anal. Chem.* **29** 1702
- [14] Oehring M and Bormann R 1990 *J. Physique Coll.* **14** C4 169
- [15] Loeff P I, Weeber A W and Miedema A R 1988 *J. Less-Common Met.* **140** 299