

Mechanically induced phase transformation in the Nb₃Au intermetallic compound

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

1991 J. Phys.: Condens. Matter 3 9319

(<http://iopscience.iop.org/0953-8984/3/47/005>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.159

The article was downloaded on 12/05/2010 at 10:49

Please note that [terms and conditions apply](#).

Mechanically induced phase transformation in the Nb₃Au intermetallic compound

L M Di and H Bakker

Van der Waals-Zeeman Laboratorium, Universiteit van Amsterdam, Valckenierstraat 65, 1018 XE Amsterdam, The Netherlands

Received 8 July 1991

Abstract. The A15 intermetallic compound Nb₃Au was subjected to grinding in a high-energy ball mill. A phase transformation from the A15 phase to the high-temperature BCC solid solution of gold in niobium was observed after milling. Differential scanning calorimetry revealed an exothermic peak with a heat content of 4.6 kJ mol⁻¹. The activation energy was 435 kJ mol⁻¹. The present result is very similar to the previous results on the V₃Ga compound. The energies involved in the order-disorder reactions for these two compounds scale very well. These results, together with similar results obtained by other authors, strongly support the concept of energy storage by ball milling mainly in the form of atomic disorder.

1. Introduction

During mechanical milling in a high-energy ball mill an intermetallic compound may transform to the amorphous state [1]. Since the amorphous state has a higher free energy than the crystalline state, an amount of free energy must be stored in the material during the milling process. There are three different sources of energy storage. In the first place it has been demonstrated that atomic (chemical) disordering takes place, i.e. during milling atoms are transferred to the 'wrong' sublattice. The type of disorder created by ball milling is characteristic of a certain compound and corresponds to the type of disorder which is also found after quenching from high temperature or after irradiation by highly energetic particles. For example, in the Nb₃Sn compound, it has been shown [2] that Nb₃Sn exhibits anti-site disorder in the early stage of milling, which means the substitution of both atomic species on each other's sublattices, whereas in the CoGa compound the disorder is in the form of triple-defect disorder [3], i.e. the formation of Co anti-site atoms in combination with the formation of vacancies on the Co sublattice.

The other two possible sources of energy storage are the formation of grain boundaries and the formation of lattice defects such as vacancies, interstitials and dislocations. Since the crystallite size may be reduced to nanocrystalline dimensions during milling, the grain boundary energy is probably more important than the defect energy. Nevertheless even with nanocrystalline dimensions the contribution of the grain boundary energy to the total stored energy may be minor if one assumes that grain-boundary energies of intermetallic compounds are of a similar magnitude to those in pure metals. At least in theoretical work [4-6] atomic disorder was considered as the major source of energy storage.

In order to shed more light upon the problem, in a previous investigation [7] we ball milled the A15 intermetallic compound V_3Ga . The idea was as follows: in the equilibrium phase diagram the A15 phase transforms to a BCC solid solution of gallium in vanadium at about 1300 °C. The fact that the BCC phase occurs in the phase diagram indicates that the (disordered) solid solution has a lower free energy than of the melt. Therefore one could speculate that the energy stored in the form of atomic disorder could not be high enough to drive the crystalline-to-amorphous transition. And indeed no amorphization took place, but instead a transformation to the BCC solid solution was observed. Even after prolonged periods of milling, the x-ray pattern remained characteristic of the crystalline BCC phase. For further evidence we present here results on Nb_3Au , an intermetallic compound which has a phase diagram in the Au-rich part very similar to that of V_3Ga .

2. Experimental procedure

The stoichiometric intermetallic compound Nb_3Au was obtained by arc melting of weighted amounts of pure niobium and gold in a purified argon atmosphere. Arc melting was repeated several times in order to obtain a homogeneous sample. The arc-melted button was crushed to small pieces. To remove mechanical stresses, and for homogenization, the specimen was annealed at 1100 °C for 1 day. Thermodynamic equilibrium was established at 700 °C by annealing at this temperature for 7 days. X-ray diffraction patterns of the annealed sample show the single A15 structure phase. 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 in the continuous pumping system keeping the vacuum at a level of about 10^{-6} torr. The starting amount of material was two grams. X-ray diffractograms were taken for the samples milled for different periods and after the x-ray measurement the powder was used for further milling. The final milling time was 60 hours. 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. Differential scanning calorimetry (DSC) measurements were carried out on a Setaram DSCIII in an argon flux to protect the sample against oxidation. The heating rates in the DSC were varied between 0.5 and 10 K min^{-1} . The DSC scan was repeated two times for each sample, the second scan was used as a blank and was subtracted as background. The superconducting transition temperature was measured by means of an AC inductive method, based on the change in magnetic susceptibility of the sample when passing from the superconducting into the normal state. The probe was inserted into a standard helium storage vessel for cooling. The temperature was measured by a carbon-glass thermometer.

3. Results

Figure 1 gives the x-ray diffraction patterns for samples milled for different periods. All the peaks from the starting material (bottom curve) can be identified as A15 structure,

showing that the sample is single phase. The lattice parameter is $5.2057 \pm 0.0006 \text{ \AA}$, not far from the reported value of 5.2024 \AA for the stoichiometric Nb_3Au compound [9], which means that our prepared sample is close to the stoichiometric composition. The superconducting transition temperature is 11.2 K , also not far from the reported value of 11.5 K for the stoichiometric compound [10]. From figure 1, it can be seen that after 10 h ball milling the sample shows a mixture of A15 and BCC structure. The intensity of A15 peaks decreases and new peaks which belong to the BCC structure appear. Upon further milling, the BCC structure quickly becomes dominant. Between 30 h and 60 h milling, the diffraction pattern does not change any more. Even after 60 h of milling traces of A15 peaks are still visible, and the diffraction peaks from the BCC structure are still sharp and clear. There is no sign that the material could become amorphous if milling is prolonged. The lattice parameter of the sample milled for 60 h with the BCC structure is $3.2767 \pm 0.0020 \text{ \AA}$. From the width of x-ray peaks in figure 1, the crystallite size can be calculated according to [11]. It turned out that the crystallite size of the sample even after 60 h milling is still of the order of 100 \AA .

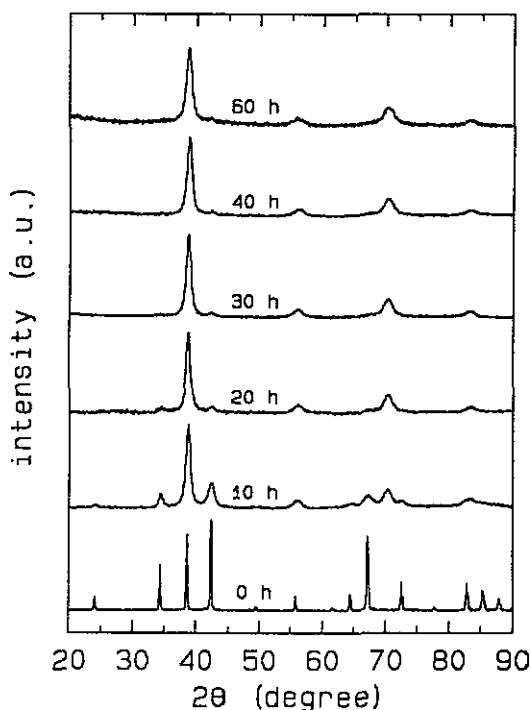


Figure 1. X-ray diffraction patterns of Nb_3Au after various milling periods.

Figure 2 shows the DSC measurements for the sample milled for 60 h. The heating rates were 2 K min^{-1} and 5 K min^{-1} . An exothermic peak was observed and the total heat effect evolved was 4.6 kJ mol^{-1} (kJ (g atom)^{-1}) for both heating rates. The transition temperature shifted to higher temperature with increasing heat rate. The shape of the transition peak seems to show the mixture of double peaks and the two peaks become more separated when the heating rate is lowered. The peak temperatures can only be determined for the second peak, which are 994 K and 1010 K for the heating rates of 2 K min^{-1} and 5 K min^{-1} , respectively. X-ray diffraction

patterns were also taken for the samples heated in the DSC with a speed of 5 K min^{-1} to temperatures of 900 K and 1050 K, respectively. The result is shown in figure 3. X-ray patterns show only BCC peaks for the sample heated to 900 K and only A15 peaks (with some small unidentified peaks) for the sample heated to 1050 K, which means that the transition peak in DSC (figure 2) corresponds to a phase transition from the BCC structure to the A15 structure. A number of heating rates, namely 0.5, 1, 2, 5 and 10 K min^{-1} were applied to measure the dependence of the peak temperatures in DSC on the heating rate. A Kissinger [12] plot is displayed in figure 4, where ϕ is the heating rate and T_m the peak temperature for the second peak. From the slope of the straight line, the activation energy was calculated as 435 KJ mol^{-1} .

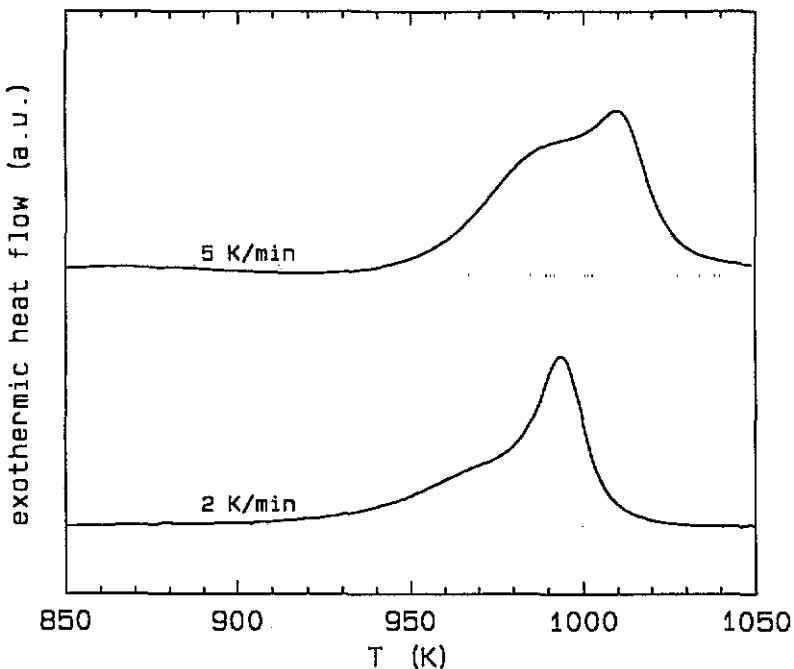


Figure 2. DSC scans with heating rates of 2 and 5 K min^{-1} for the sample ball milled for 60 hours.

4. Discussion

The results of the present investigation are very similar to previous work on V_3Ga [7], i.e. phase transformation from the A15 phase to the BCC solid solution during ball milling for both compounds. None of the materials became amorphous by ball milling. In the case of the V_3Ga compound in the composition 70 at.% V and 30 at.% Ga, we found two peaks in DSC. Preliminary results on stoichiometric V_3Ga also showed two peaks, but the first peak was considerably smaller than the second one. The shape of the DSC peaks in figure 2 indicates that a double peak is also present in this study, in particular at the lower heating rate. Here too the first peak appears to be smaller than the second one.

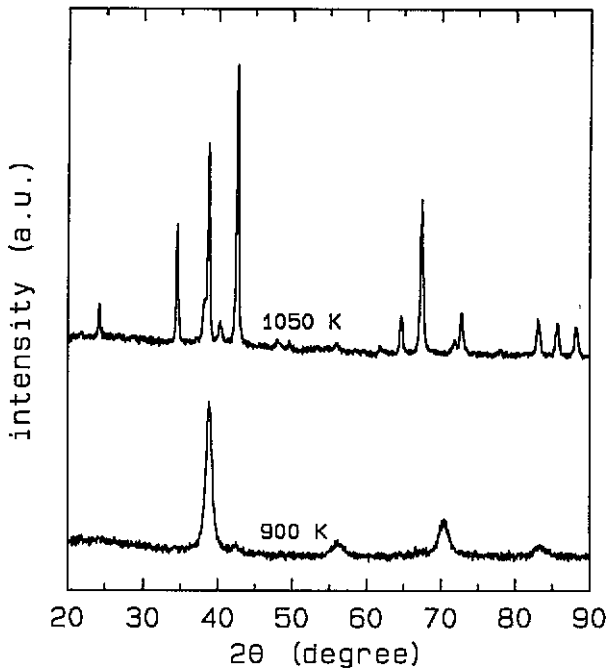


Figure 3. X-ray diffraction patterns for samples after heating to different temperatures in DSC.

The values of the total heat evolved in DSC measurement (figure 2) and the activation energy for the second peak (figure 4) for the Nb_3Au compound are higher than those for the $V_{70}Ga_{30}$ compound [7]. This is understandable from the fact that Nb_3Au has a much higher melting temperature than V_3Ga . To make a quantitative comparison, the average melting temperatures (of the solidus and liquidus) according to the phase diagram [8] for both $V_{70}Ga_{30}$ and Nb_3Au compounds, and their ratio, have been calculated and are listed in table 1. Also given in this table are the average phase transition temperatures from the A15 phase to the BCC solid solution and their ratio. It can be seen from the table that the ratios for both temperatures are very close, namely 0.82 and 0.84, respectively. It would not be surprising, if the energies measured in our experiments on $V_{70}Ga_{30}$ [7] and Nb_3Au had the same ratios as those temperatures. The ratio of the total heat evolved in the DSC by phase transformation from the metastable BCC solid solution to the A15 structure and the ratio of the activation energy for the second peak for $V_{70}Ga_{30}$ and Nb_3Au are also listed in table 1. These are 0.65 and 0.68 respectively. Remarkably, both ratios are almost equal, but different from the ratios of the above temperatures.

In different experiments we also determined the disordering energies in the highly ordered compounds. In these experiments the compounds were quenched from high temperatures, whereby a small degree of thermal disorder was introduced [13, 14]. By measuring the degradation of the superconducting transition temperature as a function of quenching temperature, we were able to evaluate the disordering energies in the compound in the highly ordered state. These disordering energies, i.e. the energies to accommodate both species of atoms on the wrong sublattices and their ratio are also listed in table 1. The ratio of these numbers is 0.72, closer to the ratios

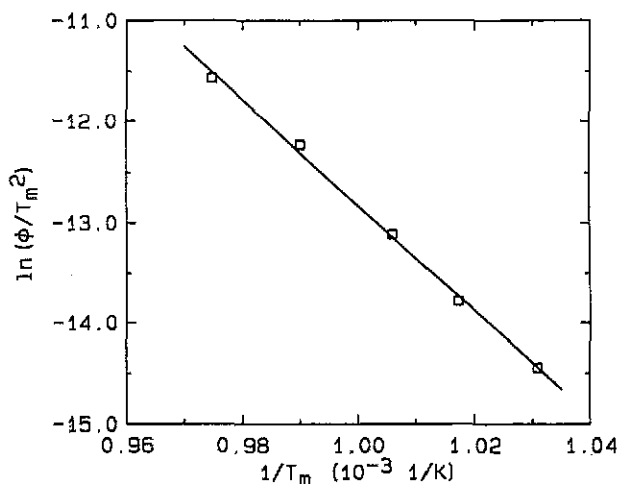


Figure 4. Kissinger plot corresponding to the second peak in DSC.

of energies measured in our experiments than to the ratios of the above temperatures. So various energies which play a role in the behaviour of both compounds are scaling rather well.

Table 1. The average melting temperatures, average phase transition temperatures, heats evolved in DSC, activation energies for the second peak in DSC and disordering energies for $V_{70}Ga_{30}$ and Nb_3Au compounds and their ratios.

	Melting temperature (K)	Phase transition temperature (K)	Heat evolved in DSC ($kJ\ mol^{-1}$)	Activation energy ($kJ\ mol^{-1}$)	Disordering energy ($kJ\ (mol\ pair)^{-1}$)
$V_{70}Ga_{30}$	1820	1510	3.0	297	119 ^a
Nb_3Au	2210	1800	4.6	435	166
Ratio	0.82	0.84	0.65	0.68	0.72

^a Disordering energy was obtained for stoichiometric V_3Ga compound.

The fact that both V_3Ga and Nb_3Au transform to the high-temperature BCC phase without amorphizing, strongly supporting the idea that the atomic disorder is the main source of energy storage during mechanical grinding. Apparently in these compounds, the disordering energy is not high enough to drive a crystalline-to-amorphous phase transformation. This is corroborated by recent work on the $L1_0$ compounds CoPt and FePt [15]. These materials transformed to the FCC solid solution during ball milling. These FCC phases are also found in the equilibrium phase diagrams of both systems. Further milling had no effect. One more example is σ -phase VFe, which transforms to the high-temperature α solid solution in a mechanical milling experiment [16]. This compound does not amorphize either. So up to now, there are five different intermetallic compounds known in which a phase transformation from the low-temperature ordered phase to the high-temperature solid solution has been observed during ball milling. In all cases, the disordered solid solution exists at high temperature in the equilibrium phase diagram and all the compounds do not amorphize upon prolonged milling periods. This makes it most probable that energy storage in the very form of disorder is responsible for the crystalline-to-amorphous transformation in those compounds that do not possess such a disordered phase at high temperatures and do exhibit the amorphization reaction. On the other hand, storage of free energy in the

form of lattice defects seems less significant for the transformation to the amorphous state: it would be surprising if these five compounds, just by coincidence were not able to store enough defect energy to amorphize.

5. Conclusions

A phase transformation from the A15 structure to the high temperature BCC solid solution of Au in Nb was observed in Nb_3Au intermetallic compound when it was subjected to mechanical grinding in a high-energy ball mill. The DSC measurement for the milled sample revealed an exothermic peak which was in fact a mixture of two peaks. It was proved that this exothermic peak is due to the phase transition from the metastable BCC phase to the stable A15 phase. The heat evolved in DSC was 4.6 kJ mol^{-1} . The activation energy for the second peak was 435 kJ mol^{-1} .

The present result is very similar to the previous result in the case of the $V_{70}Ga_{30}$ compound. The comparison of the results for the two compounds reveals that the energies involved in the ordering-disordering reactions of both compounds, i.e. the heats of transformation, the activation energies of the transformation and the enthalpies of disordering in the completely ordered compound, tally well with one another.

The present results for A15-structure intermetallic compounds in combination with results of other authors imply that the major source of energy storage in intermetallic compounds during ball milling is atomic disordering rather than lattice defects or grain boundaries.

Acknowledgments

We appreciate the help by Ir B van der Linden for the DSC measurements. The work is part of the research programme of the 'Stichting voor Fundamenteel Onderzoek der Materie' (FOM), which is financially supported by the 'Nederlandse Organisatie voor Wetenschappelijk Onderzoek' (NWO).

References

- [1] Weeber A W and Bakker H 1988 *Physica B* **155** 93
- [2] Di L M, Loeff P I and Bakker H 1991 *J. Less-Common Met.* **168** 183
- [3] Di L M, Bakker H, Tamminga Y and De Boer F R 1991 *Phys. Rev. B* **44** 2444
- [4] Johnson W L 1986 *Prog. Mater. Sci.* **30** 81
- [5] Massombrio C, Pontikis V and Martin G 1989 *Phys. Rev. Lett.* **62** 1142
- [6] Beke D L, Loeff P I and Bakker H 1991 *Acta Metall. Mater.* **39** 1259;
- Beke D L, Bakker H and Loeff P I 1991 *Acta Metall. Mater.* **39** 1267
- [7] Di L M and Bakker H 1991 *J. Phys. C: Solid State Phys.* **3** 3427
- [8] Massalski T B 1986 *Binary Alloy Phase Diagrams* (OH: Metals Park, American Society for Metals)
- [9] Powder Diffraction File, Joint Committee on Powder Diffraction Standards 1974 Set 18 (Swarthmore, PA) p 748
- [10] Vonsovsky S V, Lzyumov Yu A and Kurmaev E Z 1982 *Superconductivity of Transition Metals* (Berlin: Springer) p 262
- [11] Klug H P and Alexander L E 1974 *X-ray Diffraction Procedures* (New York: Wiley) p 687
- [12] Kissinger H E 1957 *Anal. Chem.* **29** 1702
- [13] Van Winkel A, Weeber A W and Bakker H 1984 *J. Phys. F: Met. Phys.* **14** 2631;

Westerveld J P A and Bakker H 1986 *Phil. Mag.* B 54 L15

[14] Lo Cascio D M R and Bakker H 1991 *J. Phys. C: Solid State Phys.* 3 5227

[15] Yermakov A Ye 1991 *Proc. Int. Symp. on Mechanical Alloying (Kyoto, 1991)* (Mater. Sci. Forum: Trans. Tech. Publ.) at press

[16] Fukunaga T, Mori M, Misawa M and Mizutani U 1991 *Proc. Int. Symp. on Mechanical Alloying (Kyoto, 1991)* (Mater. Sci. Forum: Trans. Tech. Publ.) at press