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Influence of milling conditions on the segregation-induced instability of Pd_3Zr

M. KIS-VARGA*
Institute of Nuclear Research of the Hungarian Academy of Sciences, 4001 Debrecen, P.O.B. 51, Hungary
E-mail: kvm@atomki.hu

D. L. BEKE
Department of Solid State Physics, University of Debrecen, 4010 Debrecen, P.O.B. 2, Hungary

A. CSIK
Institute of Nuclear Research of the Hungarian Academy of Sciences, 4001 Debrecen, P.O.B. 51, Hungary

Structural transformations in Pd_3Zr intermetallid upon ball-milling and subsequent annealing was studied under different milling conditions. The compound was milled in a medium energy vibrating mill with tungsten-carbide vial and ball as well as in a high energy planetary mill with stainless steel components. The milling processes were performed in highly purified Ar gas and in a mixture of Ar+10%H gases, respectively. The as-milled powders were annealed in the temperature range of 500–1300°C, and the structural transformations were studied by X-ray diffraction with monochromatic Cu $K_{\alpha 1}$ radiation. It is shown that the impurities introduced from milling components and the oxygen contamination from milling atmosphere strongly influence the stability of the nanocrystalline Pd_3Zr during the mechanical- and subsequent heat treatments. The evolution and coexistence of Pd(Zr) with Pd_3Zr, induced by the preparation and annealing processes, are discussed. © *2004 Kluwer Academic Publishers*

1. Introduction

It is known that nanocrystallinity can lead to the formation of a phase-equilibrium between an ordered compound and a solid solution, instead of the stabilization of a homogeneous ordered phase [1–3]. Indeed it was reported in [1] that from the initially single-phase nanocrystalline intermetallic line compound Pd_3Zr, prepared by ball-milling, an intermediate second phase of Pd(22%Zr) solid solution precipitates in a certain temperature-time window upon annealing. The phase fraction of disordered phase has a maximum by increasing temperature, and then it vanishes indicating that the system returns to the single phase ordered state. As the Zr content of Pd(Zr) was substantially lower then that in the line compound, the authors of [1] assumed that the extra Zr must have been segregated at grain boundaries or at interfaces between compound and solid solution. A phenomenological (thermodynamic) analysis showed that the two phases may coexist, and this is a necessary consequence of the large interface-to-volume ratio. In [1], the Pd_3Zr proved to be stable during ball-milling, i.e., their as-milled state was always a nanocrystalline ordered phase.

There could be another possible and simple interpretation of the formation of disordered phase from the ordered one. From an atomistic (statistical) model it was shown in [2] that with decreasing grain size (d) the order parameter decreases due to segregation effects. If during the heat treatment there is a wide distribution of d, then the order in the smallest grains can be practically zero. Thus it is expected that if the atomistic interpretation is correct, the two "phases" could have definitely different grain sizes ($d_{SS} < d_{\text{ordered}}$).

In our previous study [3] we have observed that a relatively short (46 h) milling of Pd_3Zr in a medium energy vibrating mill under vacuum gives similar results like [1]. Longer milling periods (100–300 h) however led to direct transformation of the ordered phase to nanocrystalline Pd(Zr) solid solution. The disordered phase proved to be very stable even at elevated temperatures. The extreme stability of the solid solution phase was explained by the oxidation of Zr segregated at grain boundaries. Although these experiments were performed under vacuum by continuous pumping the milling vial, the small residual oxygen content of vacuum system may contaminate the material during the long milling periods. These experiments emphasized the importance of milling conditions. In this work the nanocrystalline samples were produced under various milling conditions and the phase transformations of

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*Author to whom all correspondence should be addressed.

Pd_3Zr induced by the milling and annealing processes are discussed.

2. Experimental

The Pd_3Zr powder, product of Goodfellow Ltd., was milled with tungsten carbide vial and ball for 300 h period in a medium energy vibrating mill driven by a FRITSCH Pulverisette-0 vibrating frame ($P0$), as well as in a FRITSCH Pulverisette-6 high energy planetary mill ($P6$) with stainless steel components for maximum 30 h period. High purity Ar gas or Ar + 10%H mixture were used as milling atmosphere in both vials. The thermal stability of milled nanocrystalline phases, and their transformations induced by subsequent 24 h annealing between 500 and 1300°C were studied by X-ray diffraction with monochromatic Cu $K_{\alpha 1}$ radiation. The Zr content of Pd(Zr) solid solution was determined by fitting a straight line to the measured lattice constants given in [4]. The contamination of the milled powder from the milling tools was controlled by energy dispersive X-ray fluorescence analysis. Successive isothermal 24 h annealing at various temperatures were carried out in a vacuum furnace at 5–6 $\times$ 10^{-7} mbar.

3. Results

Our previous milling experiments [3] performed with the $P0$ medium energy vibrating ball mill under vacuum resulted always in evolution of stable nanocrystalline solid solution phase if the milling period was longer than 100 h.

The nanocrystalline powders produced by the same vibrating mill ($P0$) but in pure Ar or in Ar + H gas mixture show different behaviour upon milling and annealing as well. The result of milling in pure Ar and the phase transformations upon annealing are shown in Fig. 1.

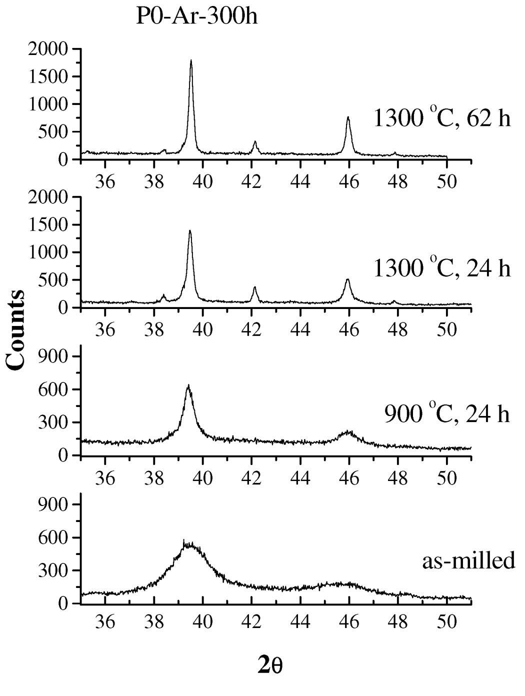

Figure 1 X-ray diffraction spectra of Pd_3Zr sample milled with vibrating mill in Ar atmosphere for 300 h.

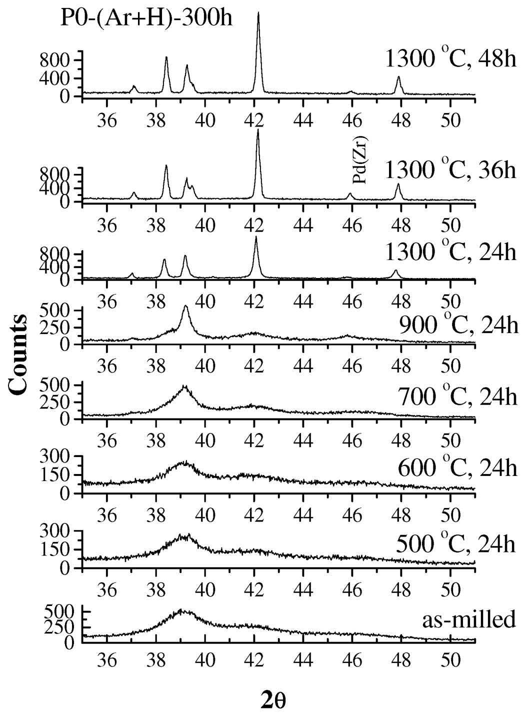

Figure 2 X-ray diffraction spectra of Pd_3Zr sample milled with vibrating mill in Ar+10%H atmosphere for 300 h.

The Pd_3Zr transforms in the mill to nanocrystalline Pd(Zr) with a mean grain size of $d = 9$ nm and $C_{Zr} = 23.5$ at.%. This phase however is not as stable against annealing as it was observed in [3]. Instead, the appearance of Pd_3Zr reflections above 1300°C at 2θ values around 39° and 42° indicates the presence of the ordered phase, too.

Filled the vial of $P0$ mill with Ar + H gas mixture, the milling leads to a nanocrystalline powder where the dominant phase is Pd_3Zr with a grain size of $d = 9$ nm. As seen in Fig. 2, a small fraction of this phase is disordered upon annealing between 900 and 1300°C, as indicated by the appearance of the (200) reflection of *fcc* Pd(Zr) solid solution at $2\theta \approx 46°$. In this temperature range the grain size of Pd_3Zr increases from 30 to 210 nm, and the Pd(Zr) grains coarsen from 10 to 140 nm with a simultaneous increase of Zr content from 17.8 to 19.8 at.% in the solid solution. After the phase fraction of Pd(Zr) reaches a maximum value of $p_{SS} \approx 0.06$ at 1300 C/36 h, it seems to vanish upon further heat treatment i.e., the system tends to return to its ordered state.

A similar but more pronounced appearance of the solid solution phase and then a complete recovery of the ordered phase was observed during heat treatment of Pd_3Zr produced by high energy planetary mill ($P6$) under pure Ar atmosphere, milled for 10 h. The mean grain size of as-milled sample is about 6 nm. It is shown in Fig. 3 that parallel to coarsening, the maximum amount of Pd(Zr) phase fraction is reached at 1000°C and this fraction is about 5 times higher than that obtained by annealing the sample produced by $P0$ vibration mill under Ar + H gas mixture. The phase transformations shown in Fig. 3 are in qualitative agreement with those described in [1], except the temperature at which the maximum amount of Pd(Zr)

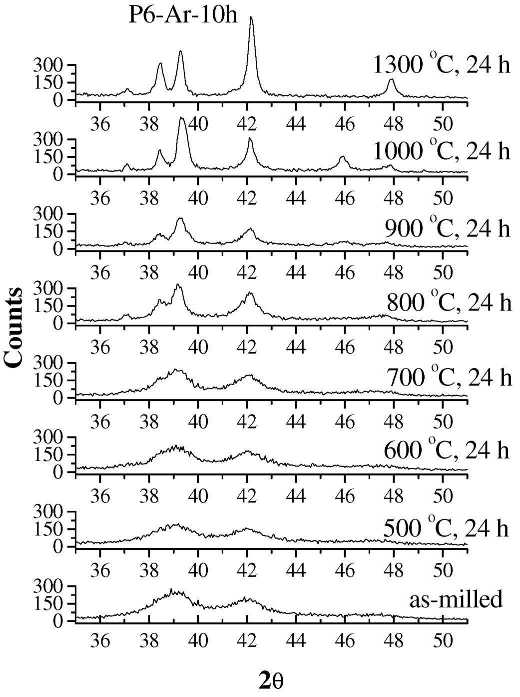

Figure 3 X-ray diffraction spectra of Pd_3Zr sample milled with planetary mill in Ar atmosphere for 10 h.

phase was observed. In our case it is higher by about 450°C.

A longer milling (30 h) in the *P*6 stainless steel high energy planetary mill introduced considerable amount of Fe contamination from the vial and balls into the Pd_3Zr. About 27 wt% Fe has been detected in the as milled powder by using EDXRF technique. According to the XRD pattern of as milled powder shown in Fig. 4, this Fe impurity might exist partly in the form of nanocrystalline ($d = 10.7$ nm) PdZr(Fe) solid solution ($C_{Zr} = 18.8$ at.%, $C_{Fe} = 8$ at.%) and the remaining Fe might segregate at grain boundaries. Upon annealing, first the Fe particles precipitate at 600°C, then by separating the Pd(Zr) and Pd(Fe) solid solution phases, a three phase mixture develops at 900°C. Finally, after a further heat treatment at 1300°C for 24 h, the Fe particles dissolute in Pd(Fe) ($C_{Fe} = 11.8$ at.%) and segregate at grain boundaries. Parallel to this transformation the reordering of Pd_3Zr also takes place. The final state of the annealing process is a two phase mixture of Pd_3Zr and Pd(Fe) phases with the excess Zr and Fe precipitated probably at grain boundaries.

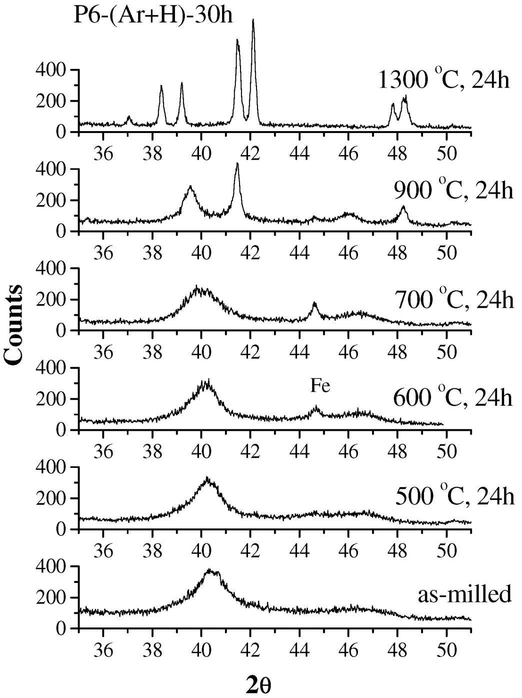

Figure 4 X-ray diffraction spectra of Pd_3Zr sample milled with planetary mill in Ar + 10%H atmosphere for 30 h.

4. Discussion

The results presented above confirm that the phase transformations of the ordered Pd_3Zr compound during the milling process and the thermal stability of the milled nanocrystalline material is strongly influenced by the atmospheric and instrumental impurities introduced to the material during the mechanical treatment. The results obtained by evaluation of XRD spectra are summarized in Table I. Milling the Pd_3Zr in a pure noble gas atmosphere for long period (signed with P0-Ar-300 h in Table I) the compound has transformed to a stable single phase solid solution. In this case, the Zr segregated at grain boundaries upon milling might be oxidized during the long preparation process by the very small amount of oxygen present even in the purified Ar atmosphere, and this stabilized the structure. After the annealing processes only a very small fraction of Pd(Zr) phase has been reordered.

In case of long time, energetic milling (P6-(Ar + H)-30 h), the instrumental contamination may dominate. It was observed that a significant amount of Fe impurity helps in disordering of Pd_3Zr during milling, and hinder the complete ordering upon annealing.

If we diminish the impurities by using short milling times, reducible (e.g., Ar + H) atmosphere and/or using less contaminating instrument components, the Pd_3Zr becomes nanocrystalline and remains ordered upon milling (P0-(Ar + H)-300 h and P6-Ar-10 h). In these cases the observed behaviour was similar to that obtained in [1] as well: upon annealing at subsequently increasing temperatures there exists a certain temperature-time window in which the ordered and solid solution phases coexist, and at high temperatures a recovery to the ordered phase took place.

The results shown in the third row of Table I (P6-Ar-10 h) are very close to those obtained in [1]. Thus one can conclude that the appearance of Pd(Zr) solid solution from nanocrystalline Pd_3Zr ordered phase, in a certain temperature-time window, is confirmed by our experiment as well. Additional interesting result is that the grain size of the Pd(Zr) solid solution is significantly lower then the value obtained for Pd_3Zr phase. A similar trend can be observed for the other milling runs as well: the average grain size of the Pd(Zr) solid solution, if once it has been formed, was always similarly smaller than that of the ordered phase. Furthermore, the final grain size of the nanocrystalline Pd_3Zr is the same within the experimental error as its grain size in

TABLE I The results of various milling runs and subsequent annealing experiments

Type of milling	Result of milling (dominant phase)	Intermediate phases upon annealing	Final state
P0-Ar-300 h (vibrating mill)	Pd(Zr), $d = 9$ nm, $C_{Zr} = 23.5$ at.%	Above 1300°C: Pd(17.4%Zr) + Pd_3Zr 83 nm 120 nm $p_{SS} \gg p_{ord}$	1300°C, 62 h: Pd(Zr) + Pd_3Zr 160 nm 1–2 μm $p_{SS} \gg p_{ord}$
P0-(Ar + H)-300 h (vibrating mill)	Pd_3Zr, $d = 9$ nm	900–1300°C: Pd_3Zr + Pd(17.8–19.8%Zr) 30–210 nm 10–140 nm $p_{ord} > p_{SS}$	1300°C, 62 h: Pd_3Zr + Pd(17.2%Zr) 220 nm 145 nm $p_{ord} \gg p_{SS}$
P6-Ar-10 h (planetary mill)	Pd_3Zr, $d = 6$ nm	900–1000°C: Pd_3Zr + Pd(17.8%Zr) 14 nm 8.2 nm $p_{SS}^{max} = 0.3$, at 1000°C, 24 h	1300°C, 62 h: Pd_3Zr 15 nm
P6-(Ar + H)-30 h (planetary mill)	PdZr(Fe), $d = 10.7$ nm $C_{Zr} = 18.8$ at.% $C_{Fe} = 8$ at.% $C_{Fe}^{total} = 27$ wt%	500–700°C: PdZr(Fe) + Fe 11–14 nm 50 nm 900°C: Pd(16.6%Zr) + Pd(11.3%Fe) + Fe 17 nm 75 nm 80 nm	1300°C, 24 h: Pd_3Zr + Pd(11.8%Fe) 68 nm 70 nm

the "phase equilibrium state" where the two phases coexist. This indicates that the recovery of the system to a single phase ordered state is not simply to increase the average grain size of the two-phase system (this is the only parameter in the model published in [1]). Instead, the solid solution undergoes a grain growth and a phase transformation to the ordered Pd_3Zr compound with the same grain size with which it coexisted. Accordingly, for the interpretation of the observed phenomenon either the segregation induced disordering, as described in [2], or a refined version of the thermodynamic model of [1] can be appropriate. Of course for a clear understanding or even for a definite decision between the two interpretations, further experiments would be desirable.

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