

From Crystal to Amorphous Transformation in $\text{Hf}_{63}\text{Pd}_{37}$ System Prepared by Mechanical Alloying

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ABSTRACT. The structural transformation from crystalline structure to amorphous structure of HfPd system prepared by mechanical alloying (MA) technique was investigated. X-ray diffraction technique was used to study structural changes with MA time. Differential scanning calorimetry (DSC) was used to study the stability of the resulting amorphous HfPd phase. A direct transformation from crystalline to amorphous phase was observed. The density of the crystalline peaks of both the hexagonal Hf and cubic Pd phases decayed exponentially as a function of the milling time. The time constants of the decaying process were obtained. On an atomic scale, the radial distribution function $\text{RDF}(r)$ and the thermal behavior of the MA $\text{Hf}_{63}\text{Pd}_{37}$ (milled for 6 h) showed that it is of a single amorphous phase.

Introduction

Amorphous alloys of the early-late transition metals attract many interesting structural investigations. These amorphous alloys used to be produced by fast quenching technique or vapour deposition on cold substrates. However, mechanical alloying (MA) is now a well-established technique^[1,2]. It is a high-energy ball milling process in which repeated mechanical mixing, cold welding, fracturing of powders occur through ball-powder collisions. Since the successful formation of the amorphous phase of $\text{Ni}_{60}\text{Nb}_{40}$ system^[2], the MA technique was applied to many other systems^[3-6].

Alloys consisting of early-late transition metals are very interesting, since amorphous phases of these high melting temperature alloys possess high crystallization temperatures^[7], and are therefore more stable.

The MA technique is a powerful technique by which an amorphous alloy can be produced at a temperature much lower than the crystallization temperature of its constituents. Although, many amorphous phase alloys of early-late transition metals have been synthesized by MA technique, Hf-based alloys have received only limited attention^[8,9]. In this contribution, the amorphization reaction in HfPd alloy prepared by MA from elemental Hf and Pd powders, was studied in terms of the structural changes as a function of time. The radial distribution function $RDF(r)$ and the DSC were used to study the real space structure and stability of the final HfPd amorphous phase.

Experimental Method

The parent powders of hafnium (99.6 wt % purity), and palladium (99.9 wt % purity) were hand mixed and then placed in a hardened steel vial of a Spex Mixer Model 8001 at room temperature, under an argon atmosphere to prevent oxidation. Samples of composition $Hf_{63}Pd_{37}$ were mechanically alloyed for 0 (parent), 0.25, 0.5, 1.5, 2.5, 3, 3.5, 4, and 6 hours. The ball of powder ratio was 4.15. For comparison purposes, another $Hf_{63}Pd_{37}$ sample was prepared. The latter sample was produced from Hf and Pd wires of 99.7 purity in the form of ingots which were then melt spun at a wheel speed of ~ 4500 rpm into ribbons in an atmosphere of purified argon.

X-ray diffraction patterns were obtained using JEOL-X-ray diffractometer and a $Cu K_{\alpha}$ target ($\lambda_{Cu} = 1.54 \text{ \AA}$). To study the real space structure of the MA HfPd system, a Mo target ($\lambda_{Mo} = 0.709 \text{ \AA}$) was used in a Philips PW 1050 vertical goniometer with a graphite curved-crystal monochromator. A DSC analyzer (TAC 7/DX Perkin Elmer) was used to study the stability of the samples at a heating rate of 30 K/min in purified argon atmosphere.

Results and Discussion

Time Constants τ of the Crystal to Amorphous Transformation

Figure 1 shows X-ray diffraction patterns for $Hf_{63}Pd_{37}$ parent and after 0.25, 0.5, 1, 1.5, 2.5, 3.5, and 6 hours of mechanical alloying. The 0 h (parent) sample shows characteristic diffraction peaks from the hexagonal Hf phase ($a = 3.1967 \text{ \AA}$, $c = 5.0578 \text{ \AA}$), and the cubic Pd phase ($a = 3.8898 \text{ \AA}$). The crystalline peaks decay as a function of the milling time. The structural transformation during the mechanical alloying does not cause any shift in the positions of the Bragg peaks and no intermediate phases can be observed throughout the amorphization reaction. This means that only one type of amorphization reactions is present in this system (at least at this particular composition). An amorphous phase is directly obtained from the starting elemental powders. Three types of amorphiza-

tion reactions have been reported in the literature. This is denoted as (type II) amorphization reaction^[4]. The systematic decay of the crystalline peaks of Hf and Pd is indicated by a systematic decrease in the intensity of the diffraction peaks accompanied by an increase in their widths as the milling time progresses.

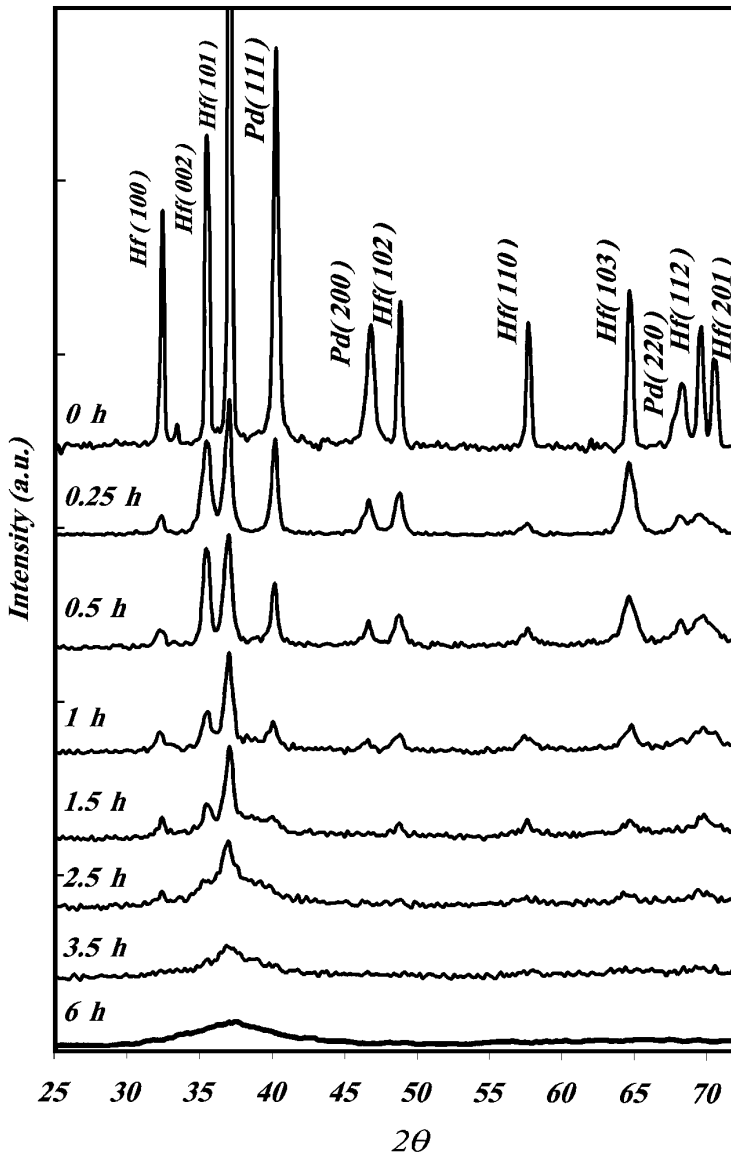


FIG. 1. X-ray diffraction profiles of the MA $\text{Hf}_{63}\text{Pd}_{37}$ samples mechanically milled for 0 h (parent sample), 0.25 h, 0.5 h, 1 h, 1.5 h, 2.5 h, 3.5 h, and 6 h.

The Bragg peaks from the Pd element decay with a faster rate than those of Hf in the early stages of the amorphization reaction and completely disappears around 2.5 hours of milling. Hf peaks, on the other hand, decay at a slower rate until they disappear at around 3.5 h of MA time. In the meantime, a broad peak starts to form at $2\theta = 37^\circ$ representing the amorphous phase. After this stage, increasing the milling time enhances the amorphous phase features and within 6 hours of milling a complete transformation from crystal to amorphous structure of HfPd system is obtained.

Finally, if the milling time is increased further, the process of amorphization will be reversed, *i.e.*, the sample will recrystallize as can be clearly seen in Fig. 2. By extending the period of milling for extra two hours after obtaining the full amorphous phase (*i.e.*, after 8 h of MA), the HfPd system shows the beginning of recrystallization. Such a retransformation from amorphous to crystalline structure has been reported in other systems^[10-12]. It is thought that the transition from amorphous to crystalline phase is due to the amorphous phase being unable to withstand impact and shear forces during prolonged MA process. This aspect of recrystallization, in this system, will be dealt with in detail elsewhere.

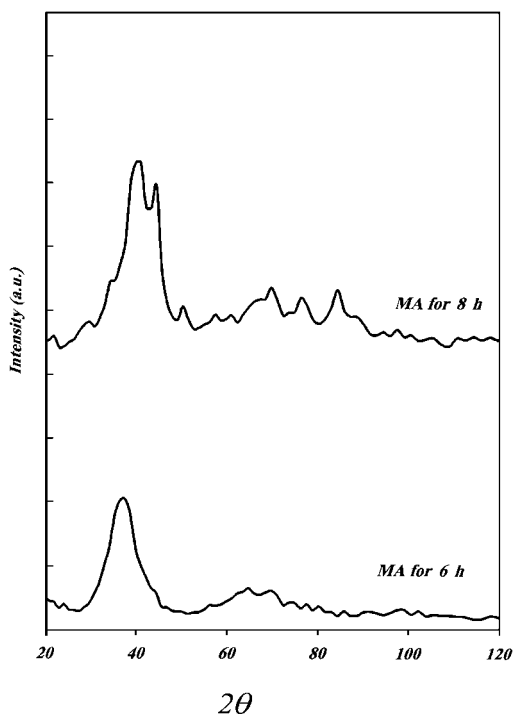


FIG. 2. The beginning of the recrystallization process of Hf₆₃Pd₃₇ sample as a result of prolonged mechanical alloying. The Hf₆₃Pd₃₇ milled for 8h is compared with the full amorphous phase obtained after 6 h of milling.

The reduction in the intensity I of the crystalline phases (decaying process) of both Hf and Pd followed a similar behavior that can be approximated by an exponential function of the form

$$I(t) = I_0 e^{-\frac{t}{\tau}} \quad (1)$$

Where $I(t)$ is the intensity of the crystalline peak at any time t during the amorphization reaction, I_0 is the intensity of the peak at $t = 0$, *i.e.*, at the beginning of the amorphization reaction (parent material), and τ is the time constant of the decaying phase, which can be defined as the time required for the intensity of the decaying peak $I(t)$ to reach $1/e$ of its initial value I_0 . The values of the intensity of the crystalline peaks were traced for a number of peaks of both Hf and Pd phases. Then the intensity of each peak was normalized as follows

$$I_{norm} = \left\{ \frac{I(t) - I_{\infty}}{I_0 - I_{\infty}} \right\} = e^{-\frac{t}{\tau}} \quad (2)$$

Where I_{∞} is the intensity of the decaying peak when it reaches its minimum value. Figure 3 shows the intensity of the normalized peak intensity as a function of the mechanical alloying time for representative peaks of Hf and Pd phases, all the other peaks behave similarly. This figure indicates that the crystalline phases of both Hf and Pd decay exponentially with milling time.

At the beginning of the amorphization reaction, *i.e.*, in the first 15 min a considerable drop in the intensity is observed. This indicates that the amorphization reaction is so fast at this very early stage, which then follows a smooth exponential function. Such a behaviour is similar to the fast decay of the crystalline peaks induced by charging hydrogen from the gas phase of ZrRh system^[13].

The decaying peaks intensities (I_{norm}) plotted on a logarithmic scale as a function of the milling time are shown in Fig. 4, for representative crystalline peaks for both Hf and Pd phases. This figure shows a very good linear relationship over the whole period of the amorphization reaction. The only exception is the very early start of the amorphization reaction (*i.e.*, in the first 15 min or so) where the reaction was found to be very fast at this early stage. Such a linearity (Fig. 4) demonstrates that the crystal to amorphous transformation in the HfPd system can indeed be expressed in terms of an exponential function as expressed in Equation (1). According to Equation (2), the time constants can be deduced. The time constants for both Hf and Pd phases deduced from the slopes of Fig. 4 are summarized in Table 1.

The average values for the time constants τ are 1.38 h and 0.69 h for Hf and Pd crystalline phases respectively. These two values show again the fast decay of the cubic Pd phase relative to the relatively slower decay of the hexagonal Hf phase.

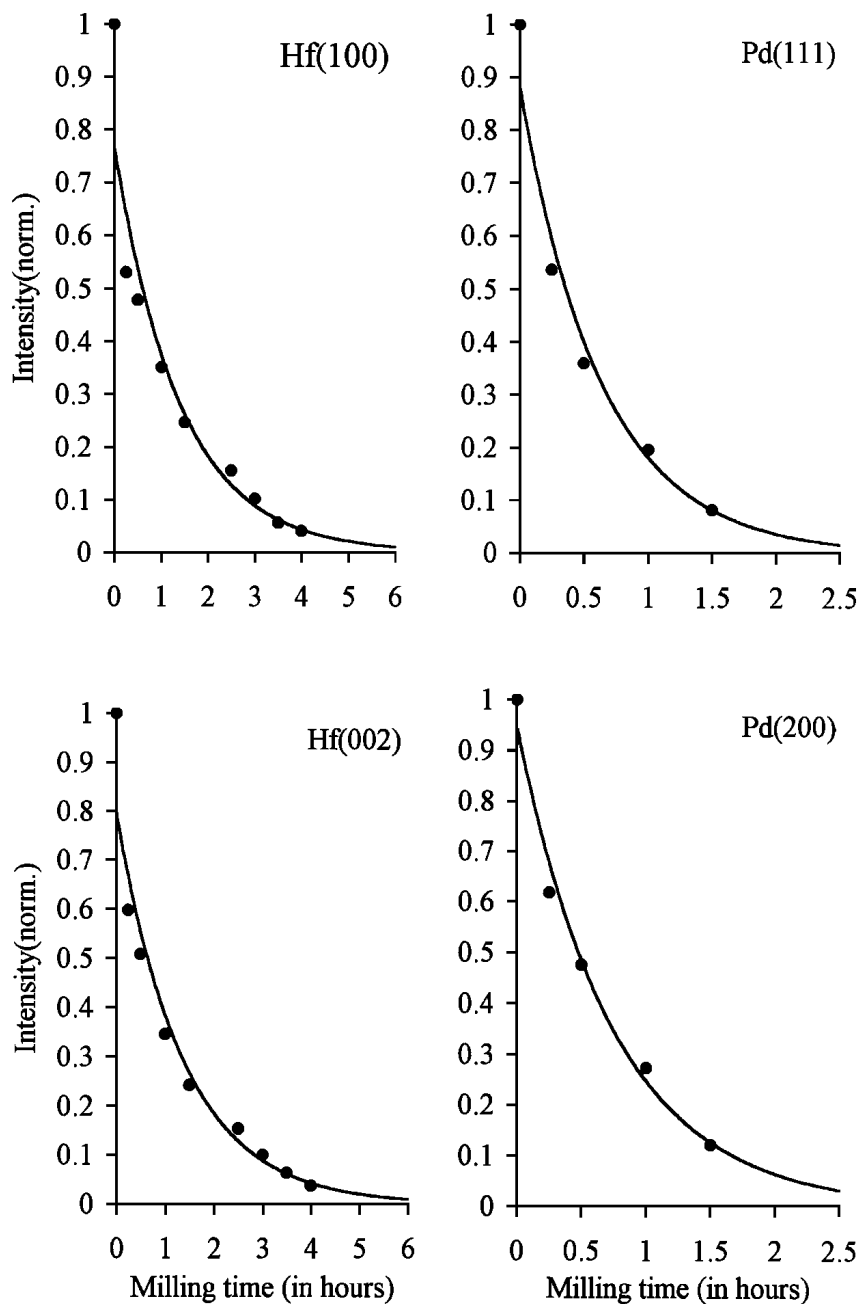


FIG. 3. The normalised peak intensity as a function of MA time (in hours). Hf(100), Hf(002), Pd (111), and Pd(200) reflections are shown. Both crystalline phases of Hf and Pd decayed exponentially with milling time.

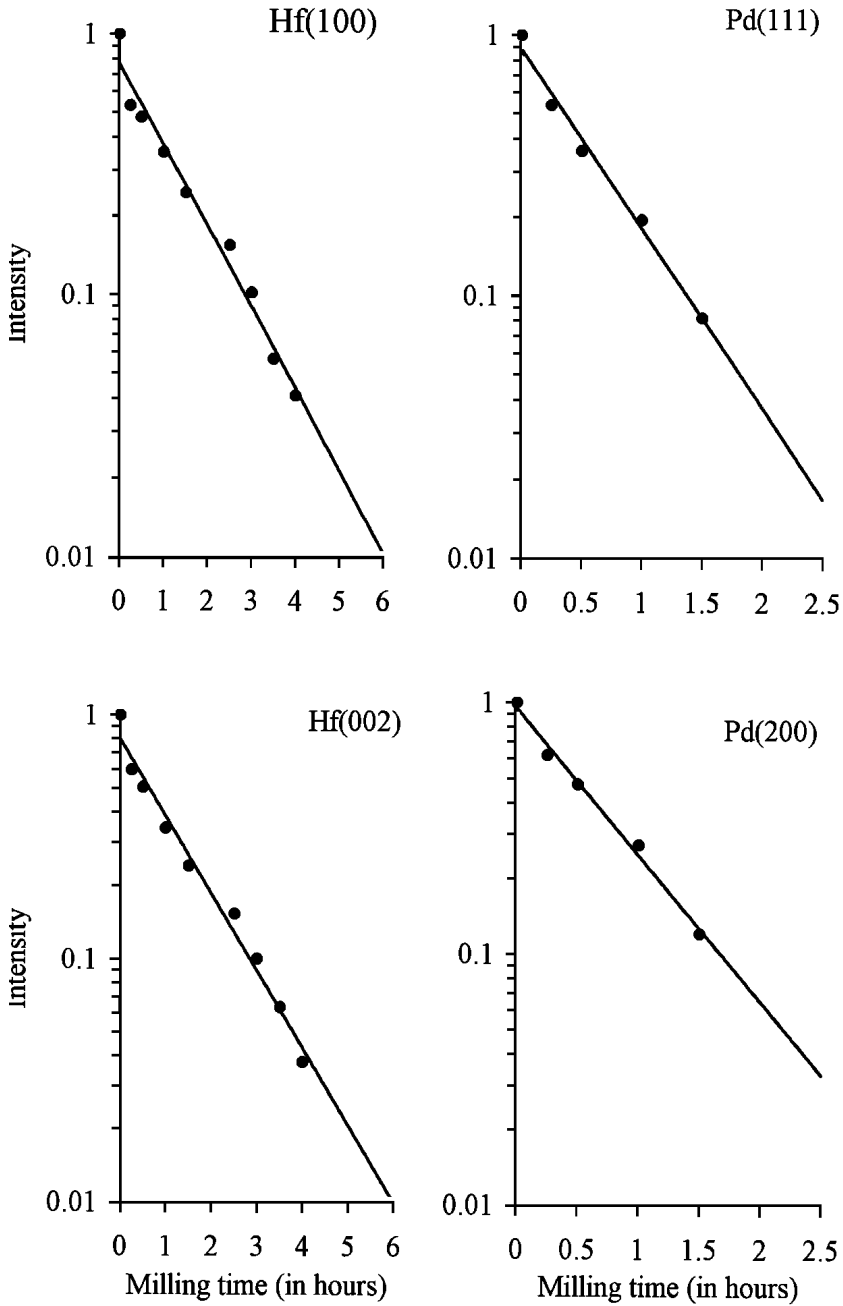


FIG. 4. The normalised peak intensity (plotted on a logarithmic scale) as a function of MA time (in hours). The time constants τ of the decaying process of the crystalline peaks of Hf and Pd phases are derived from the slopes according to Equation (2).

TABLE 1. The time constants of the decaying crystalline Hf and Pd phases, derived from Fig. 3 for representative peaks for both phases.

Time constants for the decaying crystalline phases of the $\text{Hf}_{63}\text{Pd}_{37}$ (hours)			
Hexagonal Hf phase		Cubic Pd phase	
Diffraction peak	Time constant τ_{Hf}	Diffraction peak	Time constant τ_{Pd}
Hf (101)	1.23	Pd (111)	0.63
Hf (100)	1.40	Pd (002)	0.75
Hf (002)	1.37	Pd (220)	0.68

Structure and Stability of the Amorphous Phase

To confirm that the final structure of the MA $\text{Hf}_{63}\text{Pd}_{37}$ obtained after 6 h is fully amorphous, it is compared with another $\text{Hf}_{63}\text{Pd}_{37}$ prepared by the fast quenching (FQ) technique, which is the conventional technique for producing amorphous phases. The comparison was made (on an atomic scale) in terms of the radial distribution function $\text{RDF}(r)$. This function is obtained by the Fourier transform of the total structure factor $S(Q)^{[14]}$ as follows

$$\text{RDF}(r) = 4\pi r^2 \rho_0 + \frac{2r}{\pi} \int_0^\infty Q(S(Q) - 1) \sin QrdQ \quad (4)$$

Where Q is the scattering vector, ρ_0 is the average atomic density of the sample, and r is the radial distance relative to a reference atom.

Figure 5 shows the $\text{RDF}(r)$ functions for MA and FQ $\text{Hf}_{63}\text{Pd}_{37}$ samples. The first main peak is at $r_1 = 3.05 \text{ \AA}$ and the second peak is at $\sim 5.40 \text{ \AA}$ for the two samples. Moreover, the overall behavior of the $\text{RDF}(r)$ function for the two samples is the same. Therefore, a full amorphous phase of $\text{Hf}_{63}\text{Pd}_{37}$ is obtained after 6 h of MA. This milling time is relatively short compared with other systems in the early-late transition metals^[15-17]. Similar results were obtained recently in a similar system (namely $\text{Zr}_{65}\text{Ni}_{35}$)^[12].

On the other hand, the thermal behaviour of the amorphous phase of $\text{Hf}_{63}\text{Pd}_{37}$ system is shown in the inset of Fig. 5. It shows the DSC scan for the amorphous powder milled for 6 h. An exothermic crystallization peak is found to be at a temperature of about 702 K, at this particular heating rate. No other peaks were observed in the investigated temperature range. This results confirms the $\text{RDF}(r)$ results presented above, that the structure of the $\text{Hf}_{63}\text{Pd}_{37}$ after 6 h of MA is of a single amorphous phase. Moreover, this high crystallization temperature means that the amorphous $\text{Hf}_{63}\text{Pd}_{37}$ obtained in such a way is stable.

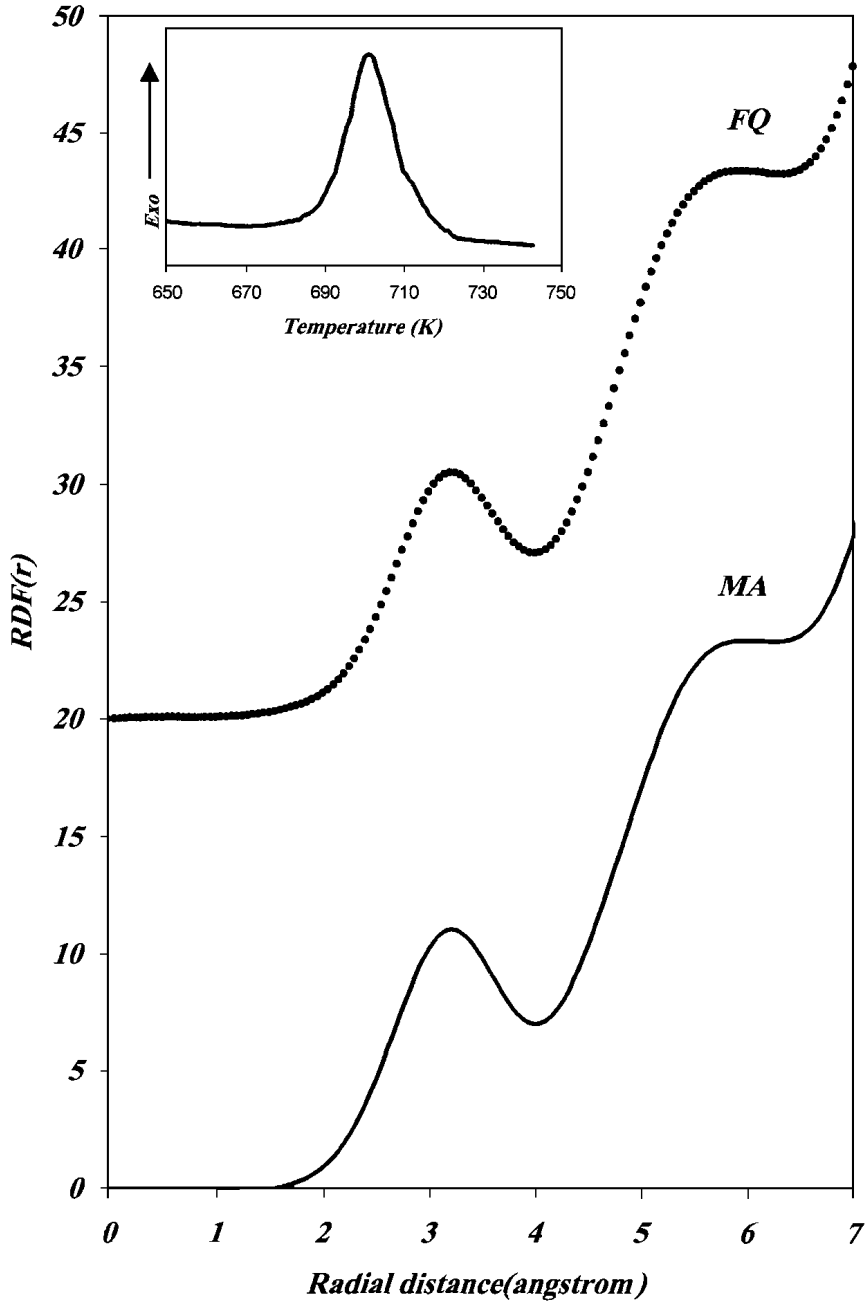


FIG. 5. The radial distribution function $RDF(r)$ for MA, and FQ $\text{Hf}_{63}\text{Pd}_{37}$ samples derived from the measured total structure factors $S(Q)$ according to Equation (3). In the inset, a DSC scan for $\text{Hf}_{63}\text{Pd}_{37}$ sampled milled for 6 h at a heating rate of 30 K/min is shown.

Conclusions

The structural transformations in HfPd system prepared from elemental Hf and Pd powders by mechanical alloying was studied as a function of MA time. Both the hexagonal Hf and the cubic Pd crystalline phases decayed exponentially. However, each phase decayed with a different rate. The time constants of the decaying processes of both phases were obtained. The average time constants are 1.38 h and 0.69 h for Hf and Pd phases respectively. A direct transformation from crystalline to amorphous phase was observed. The RDF(r) curves of both MA for 6 h and FQ amorphous Hf₆₃Pd₃₇ samples are similar, indicating that the structure of the MA Hf₆₃Pd₃₇ is of a single amorphous phase. The high crystallization temperature obtained demonstrates the high stability of the amorphous phase of HfPd system prepared by MA technique.

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من الشكل البلوري إلى الشكل غير المحدد في مركب ($Hf_{63}Pd_{37}$) المعد بالخلط المعدني الميكانيكي

علي الحجري

قسم الفيزياء ، كلية العلوم ، جامعة الملك خالد

أبها - المملكة العربية السعودية

المستخلص . لقد تم بحث تحولات البنية في نظام $HfPd$ ، المعد بطريقة السبك الميكانيكي ، خلال تحوله من البنية الأمورفية (اللاشكالية) . تم استخدام حيود الأشعة السينية لدراسة التغيرات في البنية كدالة في زمن السبك الميكانيكي . كذلك استخدم جهاز الماسح الحراري التفاضلي (DSC) لدراسة الاتزان الحراري للطور الأمورفي الذي تم استخلاصه . لقد كان التحول من البنية البلورية إلى البنية الأمورفية ، مباشراً ، وقد لوحظ أن شدة الأشعة السينية للطورين البلوريين السداسي والمكعب انخفضت على شكل دالة أسية تناقصية ، وقد تم اشتقاق الثوابت الزمنية لهذين الطورين . ومن جانب آخر ، فقد تم إثبات أن البنية الأمورفية لـ $Hf_{63}Pd_{37}$ الناتجة بعد 6 ساعات من السبك الميكانيكي وحيدة الطور ، وذلك من خلال السلوك الحراري ودراسة دالة التوزيع نصف القطرية (RDF) لهذه العينة .