

Amorphization and phase transformation of niobium pentoxide by fine grinding

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The mechanical amorphization process of Nb_2O_5 was studied. After vibro-milling well crystallized Nb_2O_5 in the H-phase for 6 h with an amplitude 20 mm, its X-ray diffraction pattern turned into a halo pattern. On prolonged grinding, however, X-ray diffraction peaks reappeared. They belonged to a new phase (TT-phase), formed as a consequence of structural restabilization. By grinding with an amplitude 50 mm, however, no halo pattern was found on the X-ray diffractogram. Instead, apparently direct phase transformation from H-phase into TT-phase was observed even after grinding for only 5 min. The effect of amplitude on the mechanochemical structural changes is discussed in relation to the crystallographical structure of Nb_2O_5 . The disorderly states of mechanically amorphized and hydrolysed materials were very alike, judging from the radial distribution function. It is therefore concluded, that a non-crystalline material very similar to a synthesized one could be obtained through a mechanical route by choosing an appropriate condition of stressing.

1. Introduction

Amorphous materials are attracting increasing interest in many industrial fields because of their diverse possibility of technical application [1]. Most of the presently available amorphous materials are prepared by a quick solidification either from a gas or a liquid phase. Several methods of producing a disordered structure from crystalline solids are also known, e.g. ion implantation [2] or solid state diffusion [3]. Because the external mechanical stress destroys the ordered crystalline state, it is also possible to obtain amorphous materials from crystalline ones through mechanical routes. There are many works on the amorphization of metallic [4], inorganic [5] or organic [6] solids. Multicomponent amorphous materials such as an amorphous mechanical alloy are also prepared in a similar procedure [7].

Comparative structural studies on the amorphous materials obtained by chemical and mechanical routes, however, are very scarce. Steinike *et al.* [8] studied the amorphization of SiO_2 through vibro-milling well-crystallized quartz. They found that more than 50% of the short-range order for the distances smaller than 0.65 nm was proved to be preserved. A subtle difference in the order between mechanically amorphized and vitreous silica even at a distance shorter than 0.4 nm was also mentioned [8]. When organic materials like cephalixin were ground, the crystallographical structure was again completely lost [9]. The information obtained from infrared spectroscopy was different, however, from that of freeze-dried amorphous material [9]. For other industrially important amorphous materials, we have not found a similar kind of comparative study between mechanically

amorphized and chemically or thermally prepared amorphous materials.

The purpose of the present study is to elucidate the process of amorphization, accompanied by comminution or grinding techniques, and characterize the state of mechanically amorphized material. For comparison, the same substance, prepared by hydrolysing NbCl_5 , with an apparent amorphous structure, was also used. Nb_2O_5 was chosen as a model substance because of its block structure from which a rapid amorphization is anticipated by investing a relatively small amount of mechanical energy.

2. Experimental procedure

2.1. Materials

Two different types of Nb_2O_5 were used, i.e. a well-crystallized one and an apparently amorphous one. Commercial Nb_2O_5 (Wako, guaranteed grade) was heated in air at 1150°C for 6 h to obtain a single stable monoclinic phase (H-phase, or "Sample H", according to the definition of Schäfer *et al.* [10]).

An apparently amorphous phase (Sample A) was obtained by hydrolysing NbCl_5 , (Toyo Soda Co., Japan). As a small amount of chlorine was occluded, the as-received sample was washed in a boiling 50% aqueous solution of nitric acid for 48 h. The washed and filtered material was subsequently heated at 380°C for 3 h under reduced pressure. Sample A showed a halo pattern in X-ray diffractometry, typical for an X-ray amorphous state. Chlorine was still contained in Sample A, up to ~3 wt%. It could only be removed by heating at temperatures above 550°C, where the crystallization simultaneously occurred.

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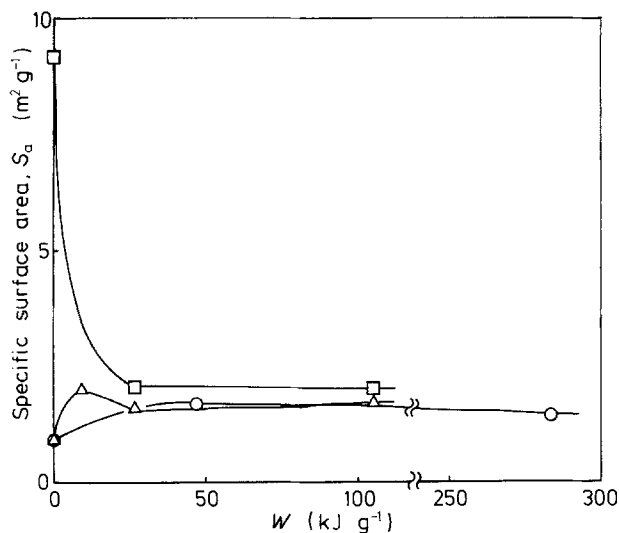


Figure 1 Variation of BET specific surface area, S_a , with applied work done, W . (○) Sample H, amplitude 20 mm; (△) sample H, amplitude 50 mm; (□) sample A, amplitude 50 mm.

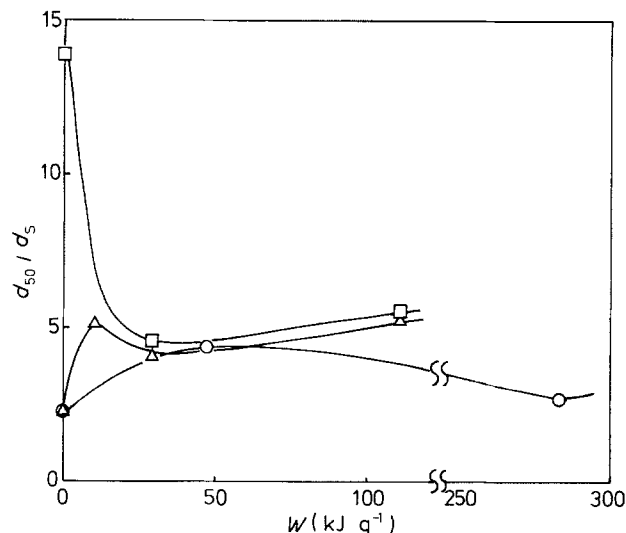


Figure 2 Variation of d_{50}/d_s with applied work done, W . (○) Sample H, amplitude 20 mm; (△) sample H, amplitude 50 mm; (□) sample A, amplitude 50 mm.

2.2. Grinding

One gramme of starting material was mechanically treated by using a laboratory-scale vibro-mill with a 50 cm³ steel vessel and 100 6 mm steel balls. Grinding was carried out with two different amplitudes, α , 20 and 50 mm, of its up-and-down motion at a constant frequency, 12 Hz. The temperature of the vessel was kept constant at 30°C with the aid of a built-in thermal jacket. The net work done during grinding was measured thermally on the principle of isoperibolic calorimetry. The details of the technique were given elsewhere [11].

2.3. Characterization of ground material

BET specific surface area, S_a , was measured by Quantasorb (Quantachrome, USA) with nitrogen adsorption. The size distribution of a particle assemblage including hard agglomerates was measured by centrifugal sedimentation (CAPA500, Horiba, Japan).

Phase analysis was carried out using conventional X-ray (CuK α) diffractometry (Rigaku, RAD-IIA, Japan) and the relative intensity of the diffraction peak was determined using premixed MgO as an internal standard. The radial distribution function was calculated by a standard method [12, 13]. Care was taken to choose appropriate conditions for background determination and smoothing. Differential scanning calorimetry (DSC, Thermoflex, Rigaku, Japan) was carried out in air at a heating rate of 10 K min⁻¹.

3. Results and discussion

3.1. Granulometrical and morphological observation

Variation of the BET surface area, S_a , with the net work done, W , for grinding is shown in Fig. 1. The specific surface area of those samples starting from H tended to increase in a similar manner when ground with different amplitudes. Conversely, sample A, with its high initial specific surface area, showed a decrease.

However, the specific surfaces at the steady state were not very different from each other.

The median particle size, d_{50} , obtained from centrifugal sedimentation was divided by the mean particle size, d_s , calculated from the BET specific surface, under the assumption of equisized spheres. The ratio, d_{50}/d_s , serves as a measure of the degree of agglomeration. As shown in Fig. 2, the ratio increased with vibro-milling time for the samples starting from H, showing that a significant amount of agglomeration took place. The tendency was the opposite for sample A. This again may be attributed to the different nature of the starting material, i.e. with a high degree of agglomeration of sample A. The state of agglomeration after prolonged vibro-milling was similar, however, to that of ground sample H, judging from the comparable value of the ratio, d_{50}/d_s .

Scanning electron micrographs of the starting as well as ground materials are shown in Figs 3a to f. As shown in Fig. 3a, the starting material, sample H, consists of rod-like particles of average length $\sim 5 \mu\text{m}$. On grinding for 3 h, rods were broken into smaller fragments of more or less equiaxial particles of 2 to 3 μm . A small amount of larger agglomerates was also observed as shown in Fig. 3b. Prolonged grinding produced agglomerates with sharper edges, the number of which increased with increasing grinding time (Fig. 3c). With an amplitude of 50 mm, edgy agglomerates were found after grinding for as little as 5 min, as shown in Fig. 3d.

The texture of sample A in the initial state is quite different from that of sample H. As shown in Fig. 3e, sample A has large, very porous agglomerates because of the preceding hydrolysis. When the sample was vibro-milled, however, the texture became similar to that of ground sample H, as shown in Fig. 3f, also containing some edgy agglomerates.

3.2. Amorphization and transformation due to mechanical treatment

The X-ray diffractograms are shown in Fig. 4. Sample

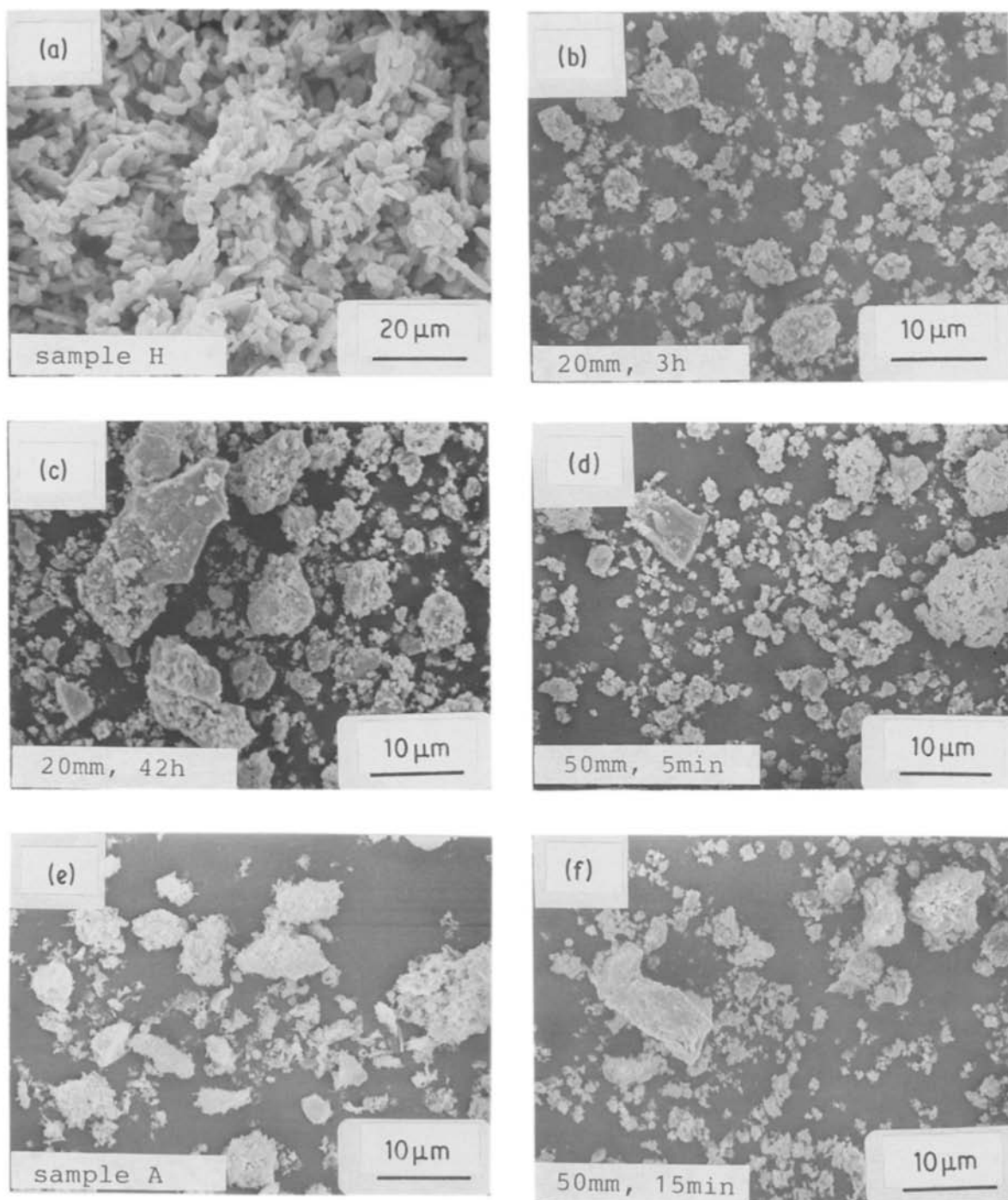


Figure 3 Scanning electron micrographs, (a) sample H, (b) sample H ground for 3 h with $\alpha = 20$ mm, (c) sample H ground for 42 h with $\alpha = 20$ mm, (d) sample H ground for 5 min with $\alpha = 50$ mm, (e) sample A, (f) sample A ground for 15 min with $\alpha = 50$ mm.

H was well-crystallized H-phase (Fig. 4a). With an amplitude of 20 mm, the X-ray diffraction peaks disappeared completely after grinding for 6 h, leaving a halo pattern (Fig. 4b). A different phase, assigned as pseudo-hexagonal TT-phase [14], was detected after 30 h grinding with an amplitude of 20 mm (Fig. 4c).

With a larger amplitude, 50 mm, broadened diffraction peaks corresponding to the TT-phase appeared almost immediately after the initiation of grinding, as shown in Fig. 4d. The intensity of these diffraction peaks increased, obviously at the cost of those of H-phase (Fig. 4e), up to 1 h grinding after which no phases other than the TT-phase were observed (Fig. 4f).

The kinetics of phase change is shown in Fig. 5, by

plotting the relative intensity of each diffraction peak, I_r , against the applied work done. Judging from Fig. 5, it would seem as if the H-phase transformed directly into TT-phase, without passing through an amorphous state, when ground with an amplitude of 50 mm. As shown in Fig. 5, the rate of crystallization into TT-phase due to grinding was lower for sample A than for the mechanically amorphized material. This might be attributed to the existence of occluded residual chlorine, which could stabilize the amorphous state.

3.3. Effects of amplitude

As described above, a larger amplitude brought about profoundly faster structural change, allowing the

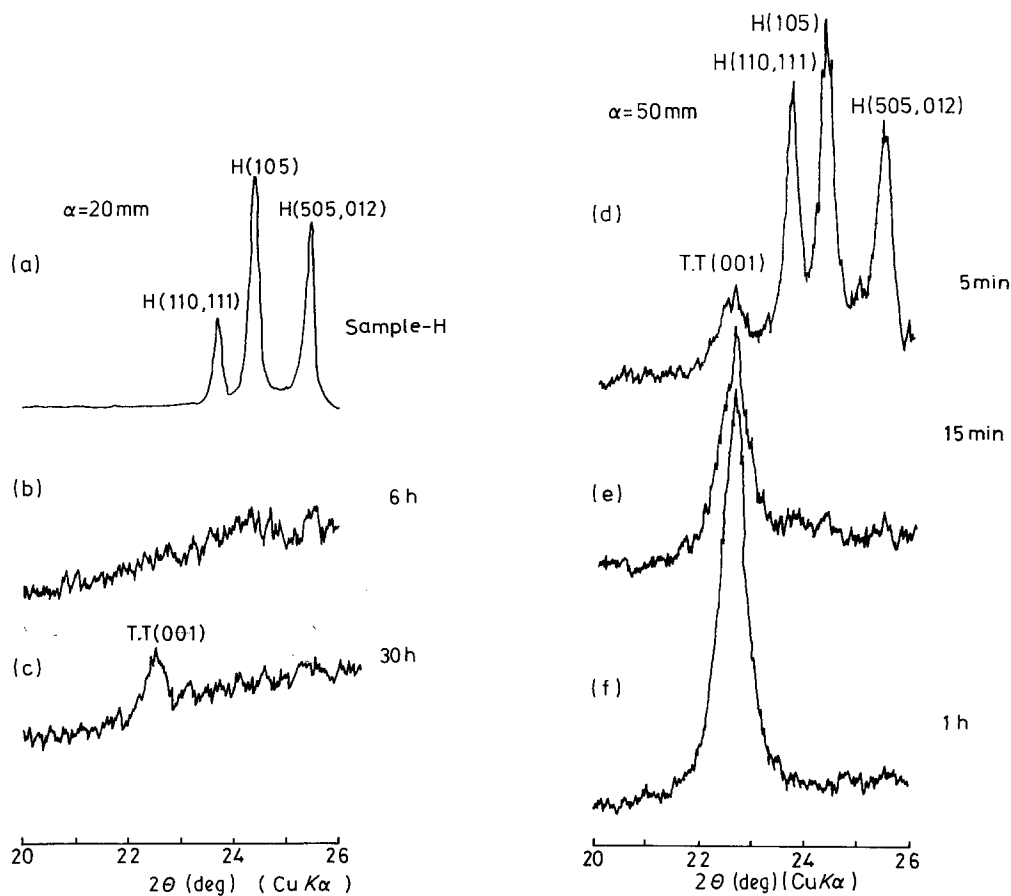


Figure 4 X-ray diffraction profiles of as-received and ground sample H, (a) as-received, (b) ground for 6 h with $\alpha = 20$ mm, (c) ground for 30 h with $\alpha = 20$ mm, (d) ground for 5 min with $\alpha = 50$ mm, (e) ground for 15 min with $\alpha = 50$ mm, (f) ground for 1 h with $\alpha = 50$ mm.

coexistence of starting H-phase and the resulting TT-phase. This leads us to the following tentative explanation based on the local difference in the micro-deformation.

Nb_2O_5 is well known for its block structure with an $\text{Nb}-\text{O}_6$ octahedron as a structural unit [15]. Because of this, the substance has a number of polymorphs, among which intimate orientational relationships exist [16]. Increasing the amplitude by a factor 2.5 intensifies the mechanical stress by a factor more than 6. This inevitably causes the structural change in a larger volume by a single impact. As a result, blocks are displaced in a larger number simultaneously, which in turn may cause a local transformation in a volume large enough to be detected by X-ray diffractometry. Compared with the same work done, a smaller amplitude means a larger number of hits with a smaller impact. This would favour a more random

orientational distribution of $\text{Nb}-\text{O}_6$ octahedra, leading to an amorphous state.

There could be an alternative explanation for the effect of amplitude. A larger amplitude may cause a larger heterogeneity of the structure, which may allow the normal amorphization process with largely different local rates. Hence, even if the unit process may proceed similarly through an apparently amorphous state and subsequent restabilization, the heterogeneity alone could cause the coexistence of H- and TT-phases, in the case of grinding with a larger amplitude. However, with a smaller amplitude, the local difference in the process of disorder and reordering of the $\text{Nb}-\text{O}_6$ octahedra must be smaller, so that the normal process progresses at similar rates everywhere, allowing no coexistence of the starting and resulting crystalline phases.

To verify the tentative mechanisms mentioned

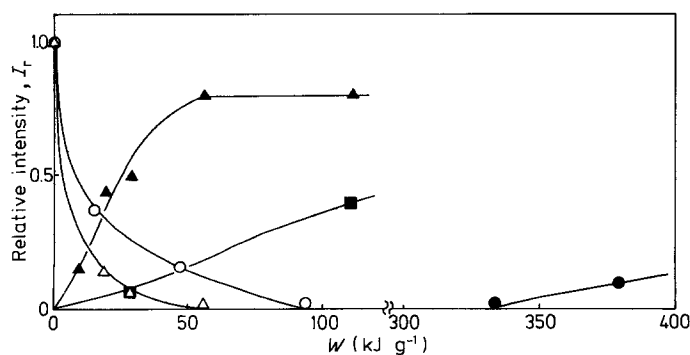


Figure 5 Change in the relative intensity of X-ray diffraction peak, I_r , with applied work done. Open symbols, H-phase; solid symbols, TT-phase; \circ , \bullet , starting from sample H, $\alpha = 20$ mm, Δ , \blacktriangle , starting from sample H, $\alpha = 50$ mm, \square , \blacksquare , starting from sample A, $\alpha = 50$ mm.

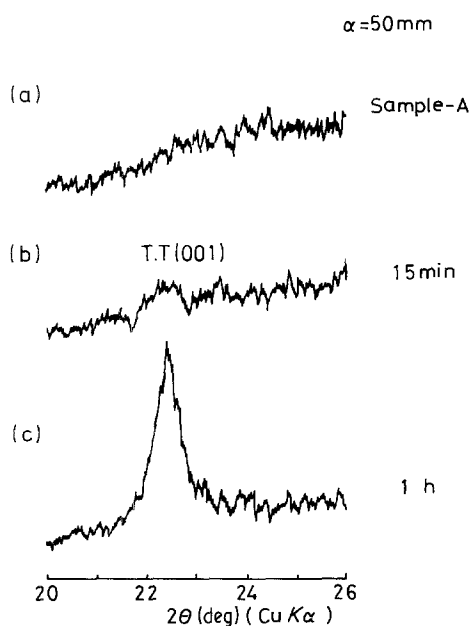


Figure 6 X-ray diffraction profiles of as-prepared and ground sample A, (a) as-received, (b) ground for 15 min with $\alpha = 50$ mm, (c) ground for 1 h with $\alpha = 50$ mm.

above, the state of microdeformation under different stress conditions should be studied in detail, keeping the importance of the local difference in the structure in mind.

3.4. Comparison of the structure between hydrolysed and mechanically amorphized materials

It should be noted that the X-ray diffractogram of sample A (Fig. 6a) shows a halo pattern similar to the ground sample H (Fig. 4b). The ground sample of A showed broadened diffraction peaks of TT-phase, as shown in Figs 6b and c, which again were very similar to those of Figs 4c and e.

RDF of the amorphous Nb_2O_5 obtained from hydrolysis (sample A) and those of the mechanically amorphized sample are shown in Fig. 7. Sample A showed the first and the second peaks at the same position as those of mechanically amorphized material. Between these two amorphous materials of different origin, no significant differences were again found for smaller RDF peaks at larger distances. Detailed interpretation of RDF for niobium oxide with varying degrees of amorphization will be given elsewhere.

This suggests that the amorphous materials with a similar extent of orderliness can be obtained either by grinding or by hydrolysis. According to DSC measurement, the heat of crystallization was 18.6 kJ mol^{-1} , which was by 9 kJ mol^{-1} less than that of mechanically amorphized material. Sample A crystallized into TT-phase at 550°C , i.e. 60°C higher than that for mechanically amorphized material. This higher stability of sample A seems to be compatible with the higher resistance to mechanochemical recrystallization into TT-phase as shown in Fig. 5. Further experimental study is required to determine whether the apparent stability of sample A is associated with the occluded chlorine.

From the above results it may be concluded that

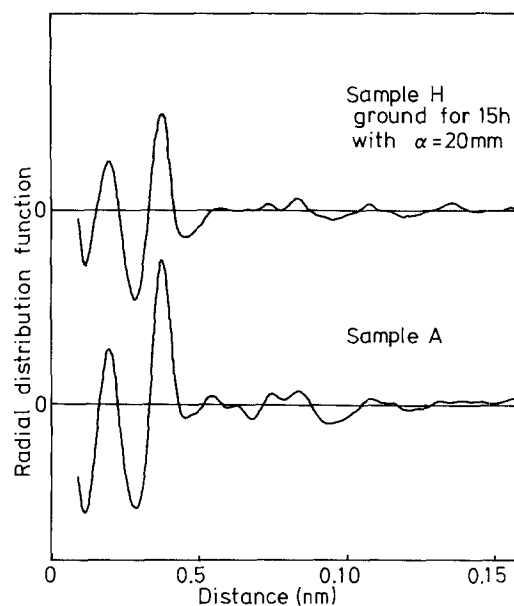


Figure 7 Radial distribution function of sample H ground for 15h with $\alpha = 20$ mm and sample A.

both the apparently amorphous materials are very similar, even on the level of crystallographical microstructure. An amorphous material similar to sample A could not be obtained, however, by vibro-milling with a larger amplitude. Thus, a mechanical treatment under carefully specified conditions can lead to an apparent amorphous state obtainable through a chemical route.

4. Conclusion

The apparent pathway of a mechanochemical amorphization and transformation depends largely on the condition of stressing. The difference should lie in the change in the local structure. By choosing an appropriate condition, it is possible to obtain an apparently amorphous material comparable to that obtained by hydrolysis or thermal decomposition.

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