JOURNAL OF MATERIALS SCIENCE 25 (1990) 5029-5035

Preparation and isochronal sintering behaviour of molybdenum disulphide compound

R. N. VISWANATH, S. RAMASAMY*
Department of Nuclear Physics, University of Madras, Madras 600025, India

The low-dimensional solid 2H-MoS_2 has been prepared by the high-temperature solid state reaction technique. Different techniques such as positron annihilation, X-ray diffraction, microhardness and scanning electron microscopy have been used to study the isochronal sintering behaviour of this compound from room temperature to 700° C. In the positron annihilation experiments, an anomaly was observed in the temperature region 400 to 500° C. The presence and reduction of stacking fault defects, changes in the void size, breaking-up of grains and transcrystalline fractures during sintering were also investigated.

1. Introduction

Molybdenum disulphide (MoS_2) belongs to the group of layered low-dimensional solids with well-established crystal structure hexagonal form determined by Dickinson and Pauling in 1923 [1]. Subsequently, a rhombohedral form of MoS_2 was synthesized by Bell and Helfert in 1957 [2], Jellinek *et al.* in 1960 [3], Zelikman *et al.* in 1961 [4] and Semiletov in 1961 [5]. The occurrence of hexagonal and rhombohedral forms in nature has been reported by several workers [6–8]. Synthesis of amorphous, hexagonal (H) and rhombohedral (R) molybdenum disulphide from thiomolybdate solution under hydrothermal conditions in an autoclave was reported by Arutyunyan and Khurshudyan [9]. The difference in the hexagonal and rhombohedral systems lies only in the way the MoS_2 layers were stacked [10].

MoS_2 is widely used in industry as a grease or dispersant or in paste form because it exhibits antifriction, wear, increasing load-carrying capacity, etc. [11]. The effect of MoS_2 concentration on friction was investigated using a compression test, and succeeded in producing lower friction materials by a suspension of MoS_2 in a light mineral oil [12]. The compaction behaviour of MoS_2 as a function of particle size and applied pressure was done by Shapiro for engineering and metallurgical applications [13]. Single crystals of 2H-MoS_2 form were grown directly from the powder compound and 3R-MoS_2 form by using any halogen gas (chlorine, bromine and iodine) as a transporting agent [14, 15]. The linear increase in the *a*-axis (parallel to the layer) and the non-linear increase in the *c*-axis (perpendicular to the layer) over the temperature range 10 to 320 K was observed by Murray and Evans [16].

A sintering technique is used in the fields of ceramics and powder metallurgy for industrial applications such as development of metallurgical tools, solar energy conversion materials, high melting temperature crucibles for crystal growth, high-quality dielectric and ferrite materials, etc. [17, 18]. During sintering, the following changes take place: (a) in the mobility of atoms, (b) in the contact surface between the particles, (c) in the mechanical properties, (d) in the nature of surface morphology and (e) recrystallization occurs [19, 20].

With an overall survey of the work carried out on MoS_2 compound as given in the above references, the sintering behaviour of this compound has been studied using different experimental techniques: (i) positron annihilation, (ii) X-ray powder diffraction, (iii) microhardness measurements, and (iv) scanning electron microscopy.

1.1. Crystal structure

MoS_2 is crystalline diamagnetic semiconductor belonging to the large family of layer-like compounds having the formula TX_2, (T = transition metals, X = S, Se and Te) whose crystal structure results from the stacking of MoS_2 layers. The layers are stacked with either one of the stacking operation screws or translations [21]. Depending upon the way in which the layers are stacked, the number of polytypes are formed. At present there are three types of two-layer structures ($2H_1$, $2H_2$ and 2T) and one type of three-layer structure (3R). The most common polytypes are the hexagonal 2H-MoS_2, where the stacking sequence is ABA|BAB in the $11\bar{2}0$ section and the rhombohedral 3R-MoS_2, where the stacking sequence is ABA|BCB|CAC in the $11\bar{2}0$ section (Fig. 1a). The basic form and the crystal structure of 2H-MoS_2 are shown in Figs 1b and c. In each stacking of MoS_2 layers, the molybdenum atoms are surrounded by six sulphur atoms forming trigonal prismatic or octahedral co-ordination depending upon the ionic ratios r_{M^+}/r_{X^-} and fractional ionic character

$$f_i = 1 - \exp[-\tfrac{1}{4}(X_M - X_X)^2] \qquad (1)$$

---

*Present address: Fellow of Alexander von Humboldt Foundation, Werkstoffwissenschaften, Universitat des Saarlandes, Fachbereich 12.1/Bau 43, D6600 Saarbrucken, FRG.

0022-2461/90 $03.00 + .12

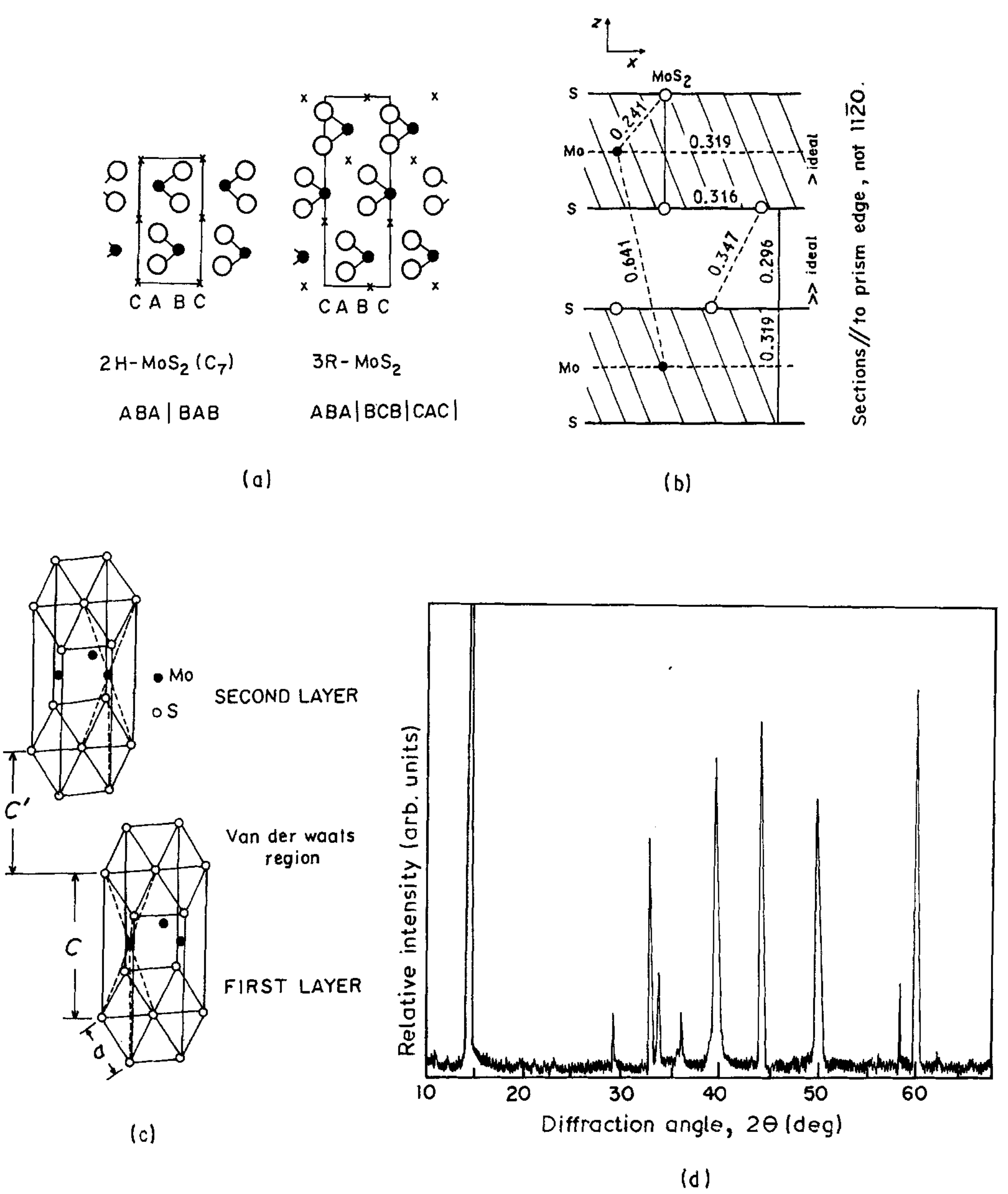

Figure 1 (a) The stacking sequence of different polytypes: 2H-MoS_2 and 3R-MoS_2. (b) The basic form of 2H-MoS_2 (not $1\,1\,\bar{2}\,0$ section). (c) The crystal structure of 2H-MoS_2 compound (a = 0.316 nm, c = 0.319 nm and c' = 0.296 nm). (d) X-ray diffraction pattern of the prepared 2H-MoS_2 compound.

where X_M and X_X are the electronegativities of the metal (M) and chalcogen atoms (X), respectively [21]. The bonding between sandwich layers is comparatively weak, because of the presence of weak Van der Waals force between the layers and a strong covalent bond within the layer. Owing to the formation of holes in the weak-bonded region, any guest metal atom can be intercalated partially or completely [22].

2. Experimental procedure

2.1. Specimen preparation

The polycrystalline compound MoS_2 was prepared by a high-temperature solid state reaction technique [23]. The starting materials of molybdenum (99.99%) and sulphur (99.999%) were taken in stoichiometric form in a silica ampoule which was sealed with a vacuum of 10^{-6} torr. The preparation of the compound was done in two steps. In order to avoid non-stoichiometry and weight loss in the resultant compound, resistive heating furnace with' uniform temperature through the length of the ampoule (15 cm) was used. First the mixture was heated at 500 ± 10° C for 24 h. Then the temperature was raised slowly to 1000° C and held there for 192 h using suitable controlling systems within ± 5° C. After heat treatment, the furnace was cooled at a rate of 30° C h^{-1}. Subsequent to this no evidence was seen for deposition of the materials and reaction with the silica ampoule. The resultant compound was in the form of shiny plate-like powder.

To confirm the phases present in the prepared compound, an X-ray powder diffraction pattern (Cu$K\alpha$ radiation) was taken (Fig. 1d) and the lines were indexed for both 2H-MoS_2 and 3R-MoS_2 systems. All the diffracted lines matched the reported values of 2H-MoS_2 well [24]. No evidence for other possible impurity phases, such as Mo_2S_3, unreacted elements of molybdenum and excess sulphur was seen.

The prepared plate-like powders were pelletized with a hydrostatic pressure of 6.4 kbar (1 bar = 10^5 Pa). The dimensions of the pellets were 1 cm diameter and 1 mm thick. Further experiments were carried out for the

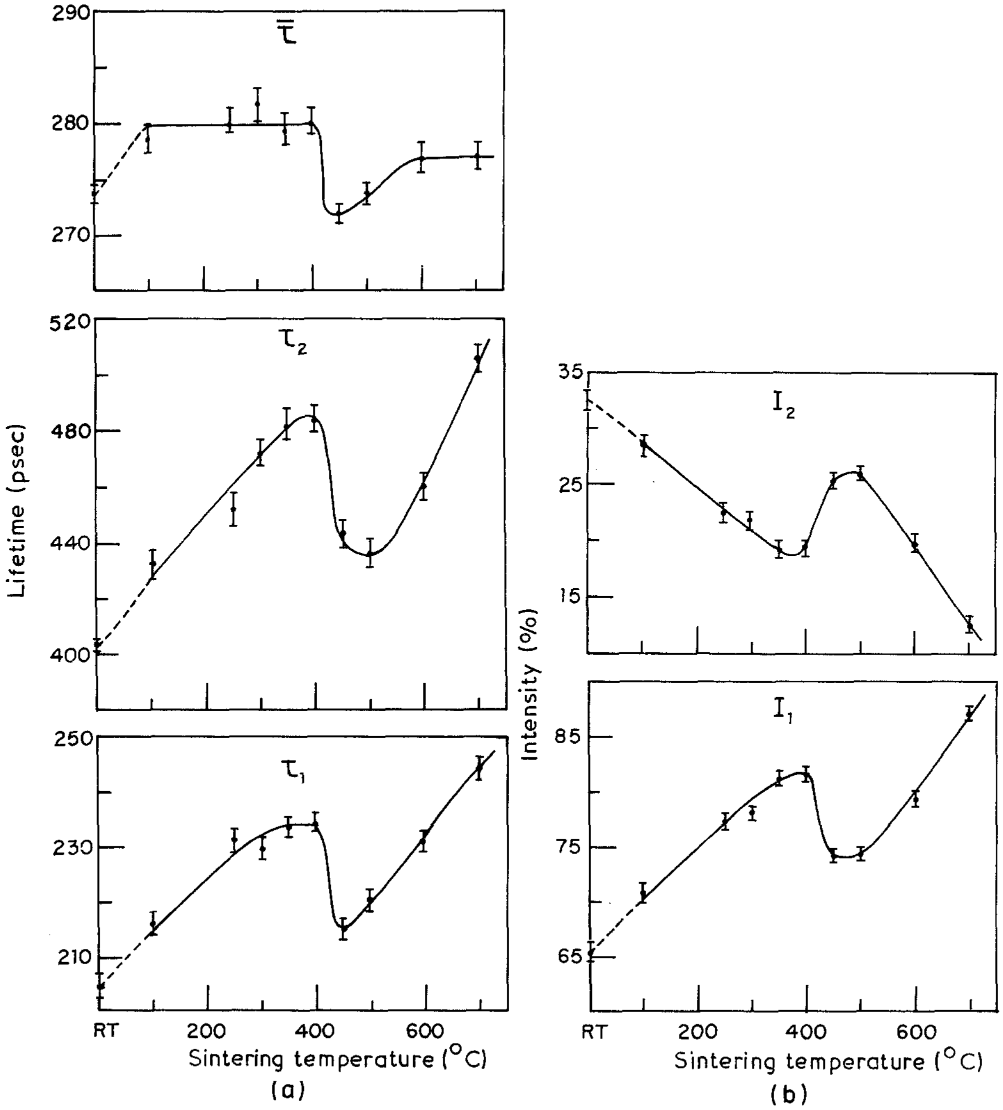

Figure 2 Positron lifetime parameters: (a) lifetime and (b) intensity of 2H-MoS_2 specimen as a function of isochronal sintering temperature.

as-pelletized specimens and for specimens sintered for 1 h at 100, 250, 300, 350, 400, 450, 500, 600 and 700° C.

2.2. Positron lifetime technique

Positron lifetimes were measured by a fast–slow coincidence system [25]. The resolution of the spectrometer was calculated using ^{60}Co radioactive isotope in the ^{22}Na energy window. The full-width at half-maximum values (FWHM) of the ^{60}Co spectrum was 260 psec.

The positron source was prepared from an aqueous solution of $^{22}NaCl$ which was deposited on a thin foil (1.13 mg cm^{-2}) and folded with a like foil, and then sandwiched between two identical specimens.

The lifetime experiments were carried out at room temperature (23° C) and the data were analysed using the POSITRONFIT program [26]. The source components were subtracted from the total spectrum during the analysis. The experimental data were fitted for two components as well as three components, after source corrections, using a MicroVAX II computer and the results were compared. In the three-term fit, the intensity of the third component was less than 1% in all cases with large χ^2 values. Hence, for further discussion, results from the two-component fit were used. The lifetime parameters τ_1, τ_2, I_1, I_2 and $\bar{\tau}$ as a function of sintering temperatures are given in Table I and graphically shown in Figs 2a and b. The average lifetime, $\bar{\tau}$, can be calculated using the relation

$$\bar{\tau} = \frac{I_1\tau_1 + I_2\tau_2}{I_1 + I_2} \qquad (2)$$

In the following section the positron annihilation results are discussed, correlating the parameters with the results of X-ray diffraction pattern, scanning electron micrographs and microhardness measurements.

TABLE I Observed positron lifetime parameters τ_1, τ_2, I_1, I_2 and $\bar{\tau}$ at different sintering temperatures

Sintering temperature (° C)	τ_1 (psec)	τ_2 (psec)	I_1 (%)	I_2 (%)	$\bar{\tau}$ (psec)
27	204	406	65.45	34.55	273.79
100	216	432	70.99	29.01	278.66
250	231	451	77.44	22.56	280.63
300	229	473	78.20	21.80	282.19
350	233	482	81.34	18.66	279.46
400	234	484	81.56	18.44	280.10
450	215	443	74.62	25.38	272.87
500	220	436	74.61	25.39	274.84
600	231	460	79.70	20.30	277.48
700	244	507	87.25	12.75	277.53

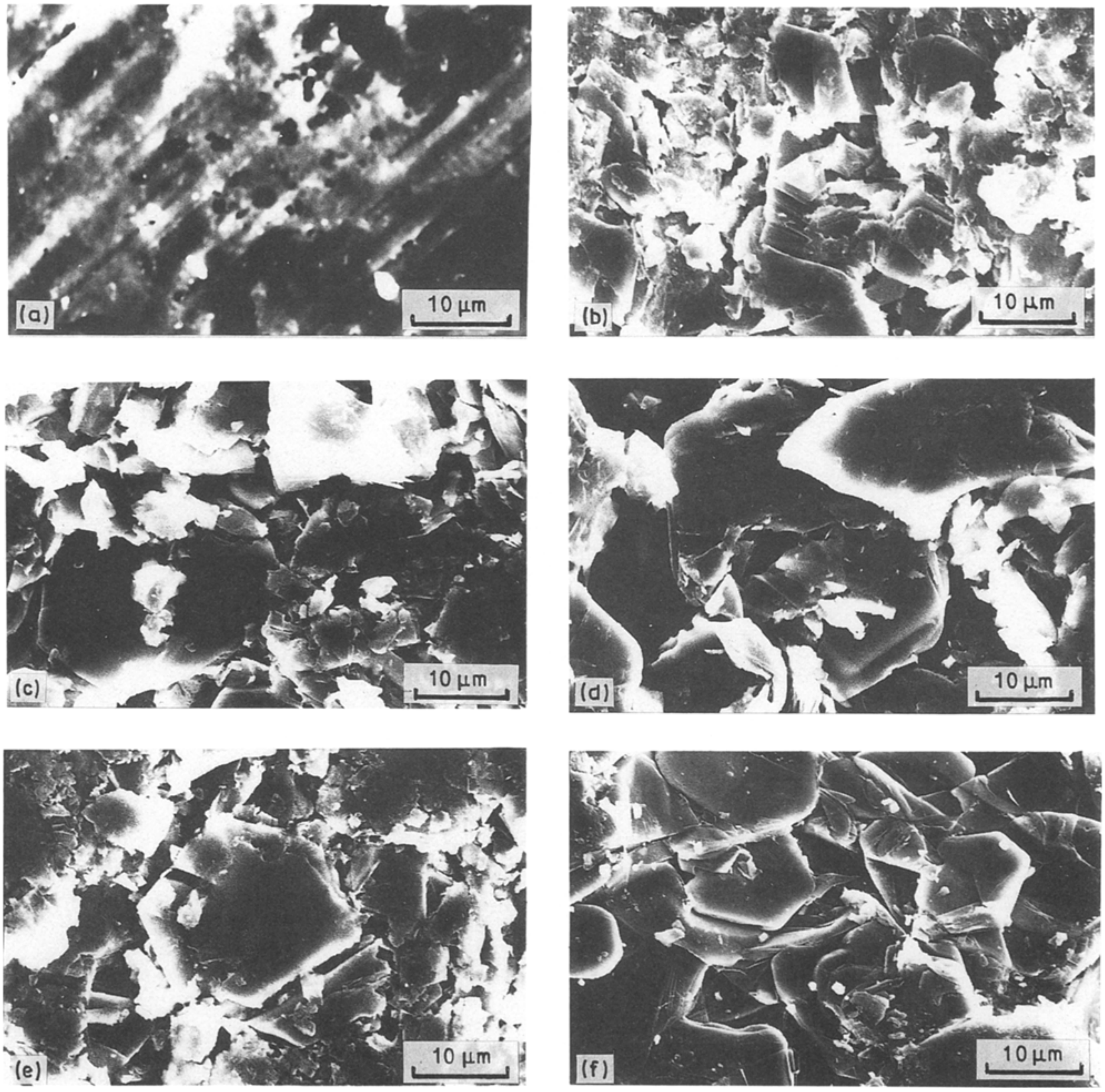

Figure 3 Scanning electron micrographs of 2H-MoS_2 specimen treated under different conditions: (a) as-pelletized, and heat treated at (b) 100° C, (c) 400° C, (d) 450° C, (e) 500° C and (f) 600° C, for 1 h.

3. Results

The prepared MoS_2 powders were in the form of plate-like grains in different dimensions with silverish black colour and shiny in nature. The surfaces of the prepared pellets were found to be in the form of a uniformly polished layer and are shown in Fig. 3a. The occurrence of these polished surfaces was due to the slipping of surface particles in certain definite planes during the applied hydrostatic pressure. The formation of this type of surface on application of hydrostatic pressure, was due to the peculiar behaviour, such as anitfriction and high brittleness, of this kind of layered compound [27].

The lifetime values, τ_1, were scattered over the range 205 to 247 psec with sintering. This may be due to the annihilation of positrons in the perfect lattice of MoS_2, as well as to lattice defects, such as structural vacancies or dislocations [28]. Thus τ_1 represents the mean lifetime of both the perfect lattice, τ_c, and structural vacancies, τ_v, or dislocations, τ_d. The values of the second lifetime τ_2 were scattered over the range 405 to 505 psec. This component can be identified as due to the annihilation of positrons in extended defects like voids (pores) [28]. Although the bound state of e^+ and $\mathbf{s}^{2-}$ or positronium formation cannot be completely ruled out, the change in the parameters indicates that the annihilation in defect sites is dominant in our samples. This is probably because of the semiconducting nature of the samples rather than ionic crystals where bound states are formed. The variation in the mean lifetime, $\bar{\tau}$, reflects the overall change in lifetimes and intensities due to variation in the type and concentration of defects [29].

Prior to heat treatment (i.e. in the pelletized specimens), the positron lifetime parameters are $\tau_2 =$ 405 psec and $I_2 = 35\%$. Up to 400° C sintering, τ_2 values increase from 405 to 485 psec and corresponding I_2 values decrease from 35% to 18%. Between 400 and 500° C there is an abrupt change (anomaly) in the τ_2 and I_2 values. From 500 to 700° C again the τ_2 values

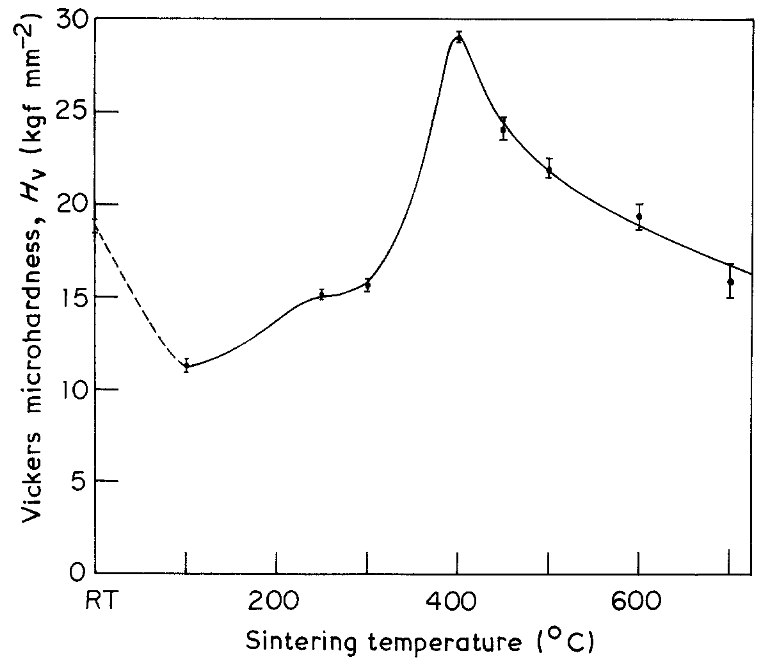

Figure 4 Vickers microhardness behaviour of 2H-MoS_2 specimen using a 100 g indentation load, as a function of isochronal sintering temperature.

increase from 436 to 505 psec and the corresponding I_2 values decrease from 27% to 15%. In order to find an explanation for the above results, the following experiments were carried out.

3.1. X-ray diffraction studies

X-ray diffraction patterns were taken for all the heat-treated samples in the pelletized form, in order to study any polymorphic phase transition (from 2H-MoS_2 to 3R-MoS_2) or structural decomposition. All the X-ray diffraction patterns were indexed and compared with the X-ray diffraction pattern of the as-prepared powders. These studies confirmed the absence of any new phases and polymorphic phase transition or structural decomposition.

3.2. Scanning electron microscopy

In order to study the grain morphology, the deformed thin layer formed on the surface of the pellets was scraped off and the images of the grains were studied using SEM; the results are presented in Figs 3b to f.

The stacking of smaller plate-like grains one upon the other in different orientations having different dimensions, is shown in Fig. 3b. At and above 400° C, the crystalline grains were broken in different directions and the images are shown in Figs 3c to e. At 600° C transcrystalline-type fractures occurred (Fig. 3f). These generally occur only in heavily strained materials and strong grain-boundary materials [30].

3.3. Microhardness studies

The results of the microhardness measurements are presented in Fig. 4. Because these materials are highly brittle in nature, the microhardness measurements were taken with an indentation load of 100 g. Above 100 g indentation load, the materials start to fracture. Up to 400°C sintering, the Vicker's microhardness value, H_v, increases and above this temperature it decreases exponentially. The explanations are given in Section 4.

4. Discussion

A number of earlier positron annihilation studies on layered compounds, such as $NbSe_3$, $TaSe_2$, and $NbSe_2$, show basically two lifetimes. Hantano *et al.* [31] reported 233 and 449 psec in $NbSe_3$ compound, 229 and 492 psec in $TaSe_2$ compound, and Dhanalakshmi *et al.* [32] reported 207 and 441 psec in $NbSe_2$ compound. These lifetimes were identified as due to the perfect lattice and point-defect annihilation (τ_1) and void (pore)-trapped state annihilation (τ_2).

In the present sample, plate-like crystalline grains were formed due to prolonged heat treatment during the preparation of the compound. Each separate grain contains a large number of randomly stacked MoS_2 layers. Due to this random stacking, a large number of stacking fault defects were produced. The presence of the random stacking of crystalline grains was verified from a scanning electron micrograph (Fig. 3b).

Up to 400° C sintering, the lifetime parameter τ_2 increases and above 400° C it suddenly drops. The microhardness value shows a peak for the sample sintered at 400° C. Increase in the microhardness is due to the increase in the packing density of the pellets on sintering. The non-linear cell expansion and the change in the energy levels due to the misplacement in stacking of atomic MoS_2 layers on heat treatment, have been reported [33, 34]. Due to the above changes, the void sizes formed in the Van der Waals region may also vary to a certain extent. The second lifetime value, τ_2, observed in the present system is of the order of the lifetime in voids [35]. Above a certain critical size of the voids (> 0.6 nm), the lifetime approaches its saturation value around 500 psec, showing that the positron wave function is concentrated in the central part of the void which is practically empty of electrons [36]. In the present study there is no evidence of annihilation of positrons in the pores formed in the intergranular region, with sizes greater than the critical value (> 0.6 nm) observed by SEM, because if the positrons are annihilated in this region the lifetime τ_2

must be almost a constant value. From the above arguments, it is felt that the increase in the τ_2 value in the temperature region 100 to 400° C may be due to the reduction of the stacking fault defects. Hence the annihilation responsible for longer lifetime τ_2, has occurred only in the voids of sizes less than 0.6 nm formed in the weak Van der Waals region. The changes observed in τ_2 are due to the variation in size of the voids, which depends on the concentration of stacking fault defects.

An anomaly was observed between the temperature region 400 and 500° C. Here the τ_2 value decreases, the I_2 value increases and the microhardness value starts decreasing. The breaking-up of grains in this temperature region was observed by SEM (Figs 3c to e). The grains were broken due to: (a) the high brittleness of this type of materials, (b) the gradient in grain sizes between the surface and bulk of the pellets, (c) nonlinear cell expansion on heat treatment, and (d) random stacking of atomic layers. Hence more voids of smaller size are formed. The reduction in τ_2 and increase in I_2 in this region shows that the positrons are trapped in the increased number of smaller size voids. The lowering of $\bar{\tau}$ and increase of I_2 in this temperature region shows that the size of voids is smaller than those present before 400° C sintering. It is not clear why the breaking-up of grains occurs only in this temperature range.

Again, above 500° C, the τ_2 value increases, the I_2 value decreases and the microhardness value still decreases. In this temperature region, transcrystalline cracks are seen in the micrographs, which cause most of the indentations to slip via the cracked regions. The changes in the τ_2 and I_2 values reflects again the amount of imperfections (stacking fault defects) present in each crystalline grain.

5. Conclusions

The following conclusions are obtained from isochronal sintering of 2H-MoS_2 compound from room temperature to 700° C.

1. The prepared MoS_2 compound contains many stacking fault defects, which occur due to the misplacement in the stacking of the atomic MoS_2 layers.

2. There is no polymorphic phase transition or decomposition of the compound until it is sintered at 700° C.

3. Void size depends on the concentration of stacking fault defects and up to 400° C sintering there is a reduction of stacking faults with reduced void concentration of increases size.

4. An anomaly was observed from the positron annihilation experiment in the temperature region 400 to 500° C which is attributed to the breaking-up of grains.

5. Above 500° C, sintering results in good stacking of MoS_2 layers but transcrystalline fracture occurs which reduce the microhardness.

Acknowledgements

The authors thank Professor V. Devanathan for his constant encouragement and support, Professor K. I. Vasu, CECRI, Tamilnadu, India, Mr G. V. N. Rao, MSD, IGCAR, India, and Professor P. Ramasamy, Crystal Growth Centre, Anna University, Madras, India for permission to use SEM, X-ray and microhardness facilities, respectively. This work was supported by the Department of Atomic Energy, Bombay, India.

References

1. R. G. DICKINSON and L. PAULING, *J. Amer. Chem. Soc.* **45** (1923) 1466.
2. R. E. BELL and R. E. HERFERT, *ibid.* **79** (1957) 3351.
3. R. JELLINEK, G. BAUERAND, H. MULLER, *Nature* **185** (1960). 376.
4. A. N. ZELIKMAN, YU. D. CHRISTYAKOV, G. V. INDENBAUM and O. E. KREIN, *Kristallogr.* **6** (1961) 389.
5. S. A. SEMILETOV, *ibid.* **6** (1961) 536.
6. J. W. FRONDEL and F. E. WICKMAN, *Amer. Mineral.* **55** (1970) 1857.
7. R. J. TRAILL, *Can. Mineral.* **7** (1963) 524.
8. A. H. CLARK, *Mineral. Mag.* **35** (1965) 69.
9. L. A. ARUTYUNYAN and E. Kh. KHURSHUDYAN, *Geokhimiya*, **6** (1966) 650.
10. F. E. WICKMAN and D. K. SMITH, *Amer. Mineral.* **55** (1970) 1843.
11. V. R. K. SASTRY, S. D. PHATAK and A. SETHURAMIAH, *Wear* **86** (1983) 213.
12. D. BHATTACHARYYA, J. N. O. COAD and J. DIXON, *ibid.* **86** (1983) 57.
13. I. SHAPIRO, *Mater. Sci.* **71** (1985) 333.
14. H. SHAFER, T. G. ROFE and M. TRENKS, *J. Solid State Chem.* **8** (1973) 14.
15. A. A. AL-HILLI, B. L. EVANS, *J. Crystal Growth* **5** (1972) 93.
16. R. MURRAY and B. L. EVANS, *J. Appl. Crystallogr.* **12** (1979) 312.
17. H. E. EXNER, *Powder Metall.* **23** (1980) 203.
18. F. V. LENEL, Powder Metallurgy – Principles and Applications" (Metal Powder Industries Federation, Princeton, New York, 1980).
19. D. L. JOHNSON, in "Encyclopedia of Materials Science and Engineering", edited by Michael B. Bever, Vol. 6 (Pergamon Press, Oxford, New York, 1986) p. 4520.
20. R. N. VISWANATH, M. A. PARVEES SAJJAD, S. RAMASAMY and T. NAGARAJAN, in "Proceedings of the International Symposium on HTSC", edited by K. B. Garg (Oxford and IBH, New Delhi, India, 1988) p. 89.
21. F. R. GAMBLE, *J. Solid State Chem.* **9** (1974) 358.
22. M. S. WHITTINGHAM, *Prog. Solid State Chem.* **12** (1978) 1.
23. J. C. WILDERVANEK and F. JELLINEK, *Z. Anorg. Allg. Chem.* **328** (1964) 309.
24. X-ray powder data file, File no. 6-0097 Powder diffraction file (JCPDS, Philadelphia, Pennsylvania, 1967).
25. D. A. GODCKE and W. J. McDONALD, *Nucl. Instrum. Meth.* **58** (1968) 253.
26. P. KIRKEGAARD, M. ELDRUP, O. E. MOGENSEN and N. J. PEDERSEN, *Computer Phys. Commun.* **23** (1981) 307.
27. M. K. AGARWAL, T. C. PATEL and H. B. PATEL, in *Proc. Ind. Nat. Sci. Acad.* **45** (1979) 392.
28. G. BRAUER, F. KERBE, Z. KAJCSOS and A. ASHRY, *Phys. Status Solidi (A)* **84** (1984) 451.
29. K. PETERSEN, N. THRANE and R. M. J. COTTERILL, *Phil. Mag.* **29** (1974) 9.
30. R. E. REED HILL, "Physical Metallurgy Principles", 2nd Edn (Affiliated East West, New Delhi, India, 1973) p. 214.
31. T. HANTANO, A. SUZUKI, K. OHTAKE, E. SATO, R. YAMAMOTO, M. DOYAMA, K. ENDO, H. IHARA, K. KANEKO and S. GONDA, in "Proceedings of the Sixth International Conference on Positron Annihilation", edited by Paul G. Coleman and Suresh C. Sharma, Leonard M. Diana (North-Holland, Oxford, 1982) p. 260.

32. S. R. DHANALAKSHIMI, T. NAGARAJAN, S. RAMASAMY, R. N. VISWANATH, A. MANIVANNAN and G. V. SUBBA RAO, *Cryst. Res. Technol.* **22** (1987) 1551.
33. M. K. AGARWAL, K. N. REDDY and P. A. WANI, *Pramana* **13** (1979) 405.
34. R. PRASAD and O. N. SRIVASTAVA, *Acta. Crystallogr.* **A27** (1971) 259.
35. V. W. LINDBERG, J. D. McGERVEY, R. W. HENDRICKS, W. TRIFTSHAUSER, *Phil. Mag.* **36** (1977) 117.
36. R. GRYNSZPAN, B. T. A. MCKER and A. T. STEWART, in "Proceedings of the Fifth International Conference on Positron Annihilation", edited by R. R. Kariguti and K. Fujiwara (Japan Institute of Metals, Japan, 1979) p. 717.

Received 24 July
and accepted 1 December 1989