ELSEVIER

Journal of Alloys and Compounds 227 (1995) 76–81

Journal of
ALLOYS
AND COMPOUNDS

Formation of the intermetallic compound VSi_2 and a VSi_2–SiC composite by mechanical alloying

L. Liu, S. Casadio, M. Magini *, C.A. Nannetti

ENEA-INN-NUMA, CRE-Casaccia, Via Anguillarese, Roma, Italy

Received 10 January 1995; in final form 2 March 1995

Abstract

Powder mixtures corresponding to the compositions $V_{33.3}Si_{66.7}$, $V_{25}Si_{50}(SiC)_{25}$ and $V_{20}Si_{60}C_{20}$ (at.%) were mechanically alloyed starting from elemental vanadium, silicon and carbon as well as silicon carbide powders. The alloying process was monitored by X-ray diffraction and thermal analysis. It was found that the intermetallic compound VSi_2 and a VSi_2–SiC composite with homogeneous and nanocrystalline structure were obtained by high energy ball milling. The opposite effect of SiC and C on the reactions between vanadium and silicon was discussed. The annealing behaviour of mechanically alloyed powders was studied by differential thermal analysis. The fast diffusion of silicon atoms into the vanadium matrix is suggested to control the solid state reactions between V and Si in the annealing processes.

Keywords: Mechanical alloying; Intermetallic compounds; Vanadium; Silicon

1. Introduction

Transition metal silicides have attracted increasing attention in the last decade due to their excellent properties, such as high melting point, low density and high resistance to oxidation. They are considered as candidate materials for replacing nickel and cobalt superalloys in high temperature (1200–1400 °C) applications [1]. Like most of the intermetallics, single-phase silicides show extreme toughness and creep strength at elevated temperature but high brittleness at low temperature, which severely limits their application as structural materials. Recent works have shown that reducing grain size and adding a second-phase reinforcing material can effectively improve their mechanical properties [2–5].

Transition metal silicides and their composites have been synthesized by various methods, such as conventional arc melting and casting, powder processing and sintering, reaction synthesis and hot pressing [6–9]. There are at least two drawbacks to these traditional techniques. First, most processes require very high temperature and industrial furnaces. Second, contaminants are usually incorporated into the material during processing and affect their properties.

Mechanical alloying (MA) of intermetallics offers a unique processing route which does not require high temperature melting. Furthermore, the process allows easy addition of insoluble dispersoids which can drastically improve mechanical properties. Various transition metal silicides (e.g. Ti_5Si_3, WSi_2, $TaSi_2$, $FeSi_2$, $MoSi_2$ and $NbSi_2$) have been successfully synthesized by MA and phase transformation in the MA process and mechanical properties of compacted materials have been studied [10–15].

As far as we know, only one paper about MA of the V–Si system has been published [16] and no investigation at all has been performed on the synthesis of VSi_2–SiC composite by MA.

In the present work, attention is further focussed on the V–Si system since VSi_2 intermetallic compound and VSi_2-based composites are promising materials for nuclear industry applications due to their low activation under irradiation. To circumvent the limitations of conventional metallurgical processing, VSi_2 and VSi_2–SiC composite have been directly synthesized through MA. The structural evolution of ball-milled alloys has been studied by X-ray diffraction (XRD) and differential thermal analysis (DTA).

2. Experimental details

Powders of vanadium, silicon, graphite and silicon carbide with a purity of 99% or higher and particle size in the range 100–300 μm were used in the present work. The compositions studied are listed in Table 1. The mixtures and steel

---

* Corresponding author.

SSDI 0925-8388(95)01626-0

Table 1
Compositions (atomic ratios) of starting materials

System	Composition
MA1	V:Si = 1:2
MA2	V:Si:SiC = 1:2:1
MA3	V:Si:C = 1:3:1

balls (10 mm in diameter) were sealed inside the cylindrical steel vials with a ball-to-powder ratio of 10:1. The MA process was performed in a planetary ball mill (Fritsch Pulverisette 5) at a rotation speed of 280 rev min^{-1}. In order to avoid oxygen and nitrogen contaminations, all the operations, i.e. loading and sampling, were carried out inside an argon-filled glovebox and the vials were sealed under argon overpressure (about 1.5 atm). The vial temperature was kept constant during milling by air cooling. At different milling times, a small amount of material was removed for XRD and DTA analyses. X-ray investigations were performed on a SEIFERT diffractometer (PAD VI) using Mo Kα radiation (λ = 0.07107 nm). Thermal analyses were done with a NETZSCH-413 differential thermal analyser with a heating rate of 20 °C min^{-1} and under high purity helium flow of 100 cm^3 min^{-1}.

3. Results

3.1. Structural evolution during MA

XRD patterns taken at various times for MA1, MA2 and MA3 are shown in Figs. 1(a), 1(b) and 1(c) respectively. In the initial milling stage, MA causes a considerable broadening of V and Si diffraction lines in the MA1 system (Fig. 1(a)) due to refinement of crystal size and increased network strain. After 6 h of milling, a few new peaks corresponding to VSi_2 appear and gradually increase in intensity with milling time. V and Si reflections totally vanish after 30 h of milling, indicating that the alloying process is almost complete. Similar phase transformations occur in the MA2 system too (Fig. 1(b)). It is interesting to note that, by adding SiC to the basic composition, VSi_2 formation is enhanced. In fact, some VSi_2 is already present after 3 h of milling and phase transformations are completed after 10 h of milling. Extended milling up to 60 h causes no significant changes in XRD pattern. The SiC diffraction peaks show no change except for a slight broadening during the whole milling. On the contrary, the alloying process between V and Si is considerably delayed in the MA3 system due to the addition of carbon (Fig. 1(c)). Although reflections of carbon vanish very quickly (1 h of MA), VSi_2 phase cannot be detected until after 10 h of milling. Further processing then leads to a gradual increase of VSi_2 and decrease of the starting elements. Residual V and Si peaks completely disappear after 60 h of milling. It is significant to note that, at this stage, some very weak peaks indexed by SiC can also be detected and its reflections become more pronounced when milling is extended up to 100 h. This means that VSi_2–SiC composite has been directly produced by MA starting from elemental powders.

Table 2
Mean crystallite size of VSi_2(112) in samples after 60 h of milling and DTA treatment

System	Crystallite size (nm)	
	As milled	After DTA
MA1	5.7	54.7
MA2	5.5	26.3
MA3	6.1	30.8

Based on the linewidth of diffraction peaks and Scherrer formula, the mean crystallite size of VSi_2 formed after 60 h of milling was evaluated. The results are given in Table 2. The obtained VSi_2 in all three systems possesses a nanostructure with crystallite size less than 10 nm.

3.2. Annealing behaviour of milled alloys

The annealing behaviour of mechanically alloyed products at various milling times was investigated by DTA; results are presented in Figs. 2(a)–2(c). It is found that the shape of the DTA curves significantly changes with milling times and starting compositions.

For the MA1 system (Fig. 2(a)), an exothermic peak in the range 990–1100 °C with a broad shoulder just before the peak is observed for the sample milled for 1 h. After 6 h of milling, the peak and shoulder become negligible, while another significant peak between 540 and 720 °C appears. This low temperature peak increases with milling time up to 10 h, then decreases and vanishes after 60 h of milling. In the case of the MA2 system (Fig. 2(b)), the DTA scan for the sample with 1 h of milling shows a broad exothermic signal in the range 540–660 °C. It becomes stronger after 3 h of milling, then gradually decreases and totally disappears at 30 h of milling. As far as the MA3 system is concerned (Fig. 2(c)), an exothermic peak in the high temperature range 1000–1150 °C is again found for the sample milled for 1 h; after 6 h of milling, the high temperature peak completely disappears and another peak between 680 and 860 °C begins. Similarly to the MA1 system, this peak first increases and later decreases with milling, showing a maximum at 10 h. Moreover, this peak continuously shifts towards lower temperatures with increasing milling times and still exists after 60 h of milling.

All the samples treated by DTA were examined by XRD. For the samples milled for rather long times (i.e. 6 h or more for the MA1 and MA2 systems and 10 h or more for the MA3 system), DTA treatment always leads to formation of expected equilibrium phases, namely, VSi_2 for MA1 and VSi_2–SiC composite for MA2 and MA3. Fig. 3 shows the XRD patterns of the samples milled for 60 h after DTA as typical examples. It can be seen that the XRD patterns in

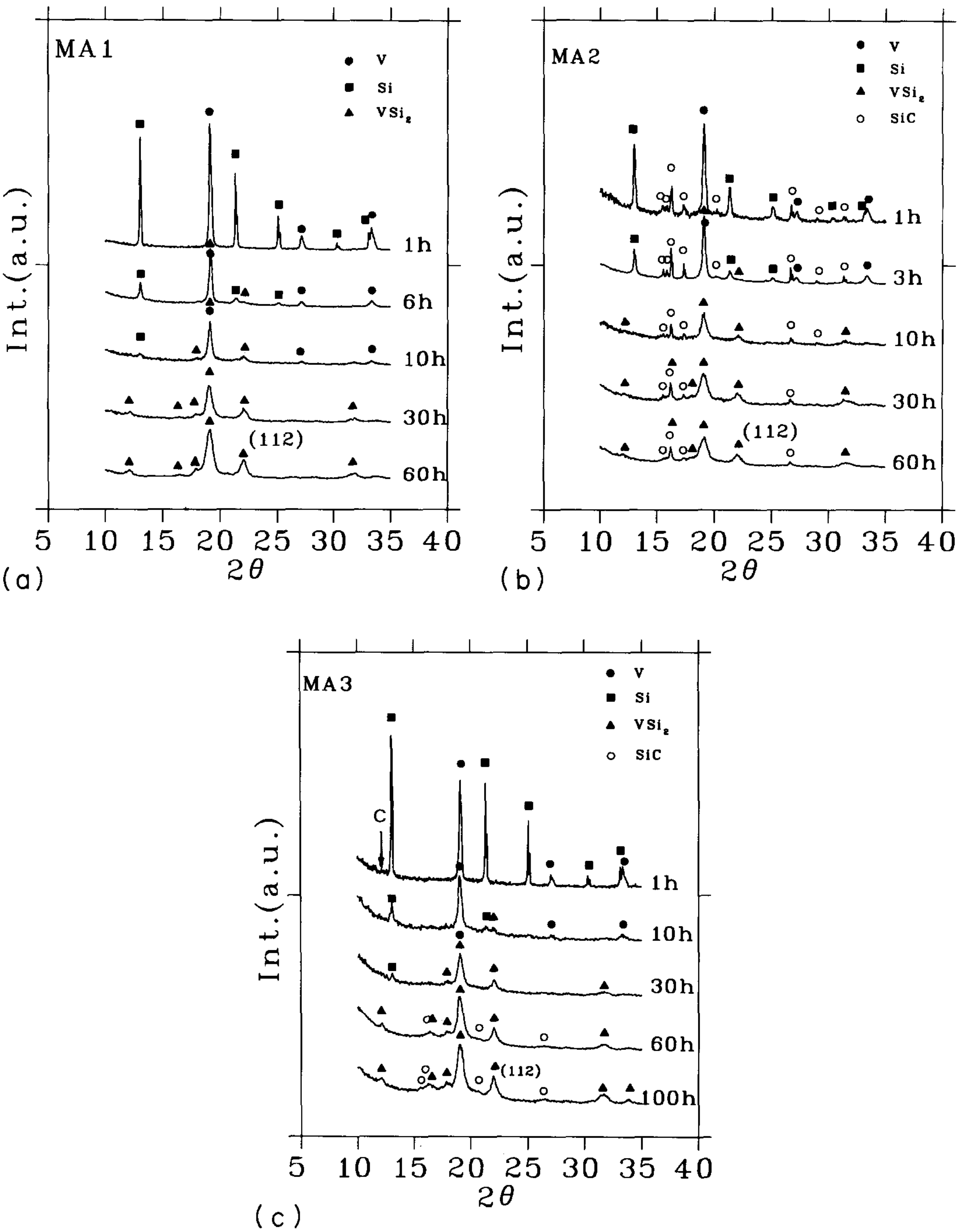

Fig. 1. XRD patterns of the three powder mixtures after different milling times: (a) MA1 system; (b) MA2 system; (c) MA3 system. The position of the strongest reflection of graphite is illustrated in (c).

curves b and c are very similar, confirming thus that the VSi_2–SiC composite can be directly formed from elements by ball milling. The Scherrer formula was applied to check the crystallite growth after annealing, for comparison with as-milled alloys. VSi_2 formed by 60 h of milling and thermally treated by DTA was analysed according to the profile of the (112) X-ray reflections shown in Fig. 3. The results are also presented in Table 2. The smaller crystallite size in MA2 and MA3 samples than in the MA1 samples suggests that the SiC presence (added or formed) remarkably suppresses grain growth in the annealing process.

For the samples milled for less than the above-mentioned times, DTA causes an incomplete reaction between elemental components and formation of some V-rich silicides (such as V_5Si_3 and V_3Si) in addition to the expected equilibrium phases. The XRD results for the sample milled for 1 h after DTA are presented in Fig. 4 as an exemplification. The final products of the MA1 sample are VSi_2, a little amount of V_5Si_3

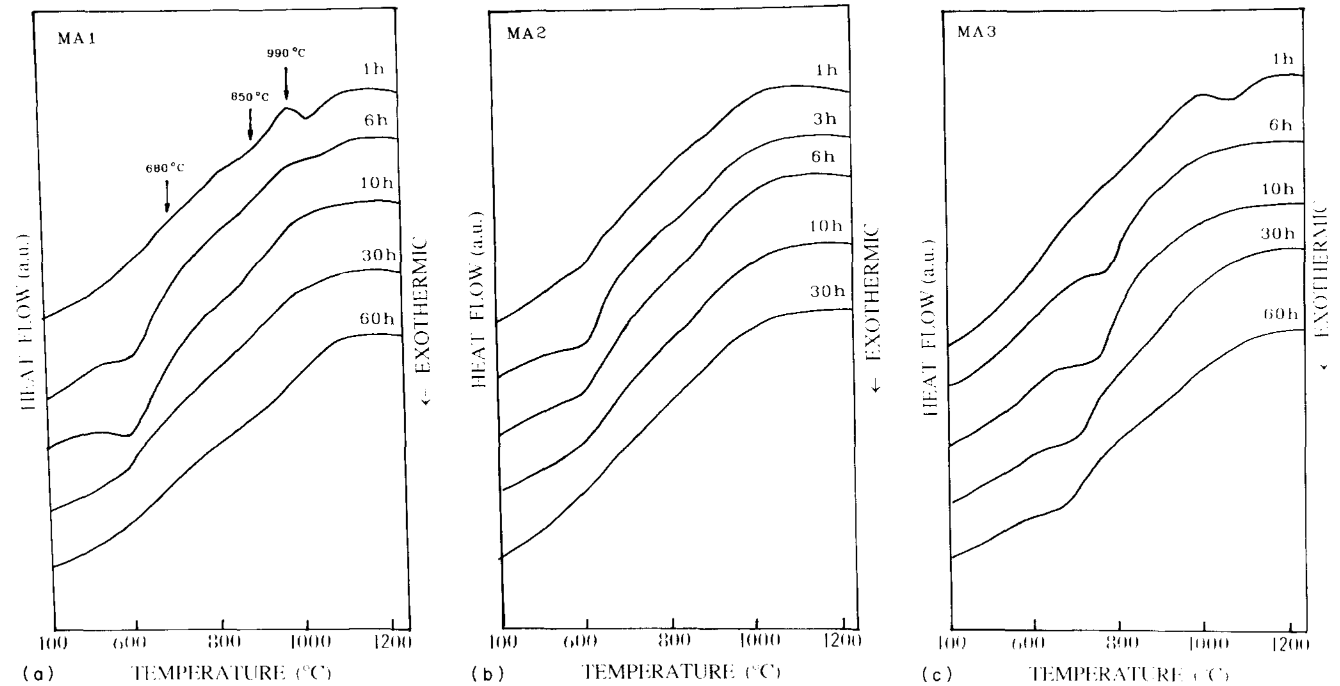

Fig. 2. DTA traces of the three powder mixtures after different milling times: (a) MA1 system; (b) MA2 system; (c) MA3 system.

as well as residual Si. The V-rich phase V_5Si_3 becomes more significant for MA2 and particularly for MA3 samples, where V_5Si_3 is the dominant phase formed. Additionally, a little amount of V_3Si and VC was also found in MA2 and MA3 samples respectively. For the three systems, with increasing milling time, DTA causes a decrease of these unexpected phases and residual Si until they completely disappear.

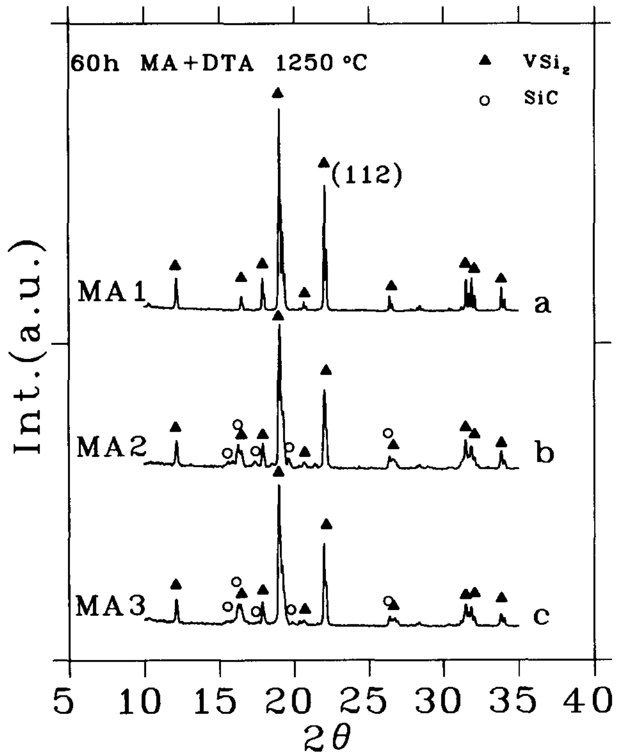

Fig. 3. XRD patterns of the three systems milled for 60 h and heated to 1250 °C for DTA.

4. Discussion

It is accepted that solid state reactions (SSRs) in MA originate from interdiffusion at the fresh interfaces between components [17,18]. At the initial stage, MA always causes a fragmentation of particles by repeated cold welding and fracturing. As a result, a high density of fresh interfaces is created, and SSRs can start up. It follows that the ability to create fresh interfaces in an A–B binary system under milling should play an important role in promoting SSRs. Addition of a third component, in general, would slow down SSRs because it reduces the possibility of A–B combination. However, a positive effect can also be encountered if the added material is brittle. In fact, at microscopic level, it may act as a wedge promoting fracture of the particles and consequently enhancing the SSRs. This is just what we have found in the MA2 system where a brittle ceramic compound has been added to the V–Si mixture. Its addition has undoubtedly promoted the fragmentation of elemental particles and accelerated the alloying process. The opposite effect is registered by adding the soft graphite powders. In this case the ultimate effect will only reduce the possibility of recombination between V and Si with the overall effect of delaying their SSRs.

In order to investigate the interdiffusion of V and Si and the phase transformations during annealing, the sample of the

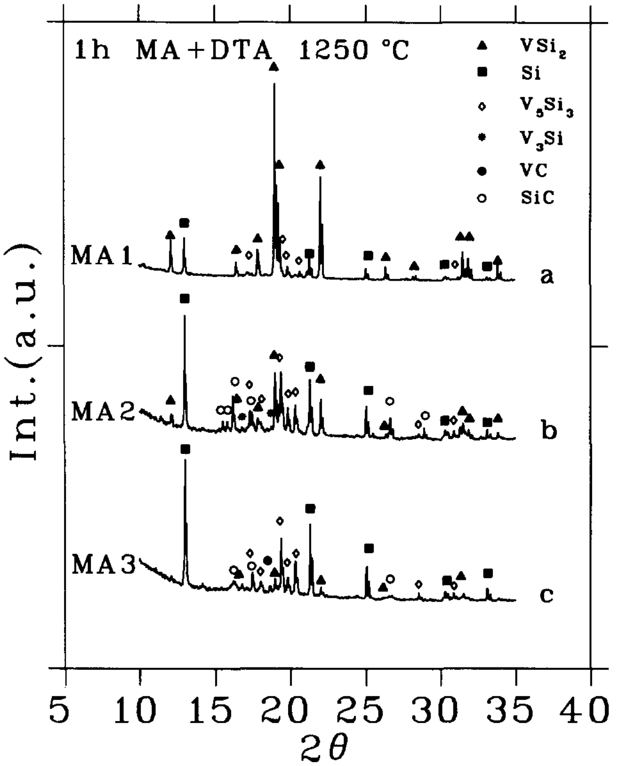

Fig. 4. XRD patterns of the three systems milled for 1 h and heated to 1250 °C for DTA.

MA1 system milled for 1 h was examined by XRD after DTA treatments at increasing selected temperatures (indicated in Fig. 2(a)). The reason for choosing this sample is that the basic reaction between V and Si is not disturbed by other components. Further, the short milling time, while ensuring the intimate mixing of the components so that they are prone to react, has not yet promoted any formation of new phases whose growth can therefore be followed by thermal treatment.

Fig. 5 shows the XRD patterns for the MA1 sample milled for 1 h and thermally treated by DTA to different temperatures. Heating the sample to 680 °C firstly causes the formation of a little amount of V_3Si compound with a decrease of vanadium reflections. Increasing annealing temperature to 850 °C promotes the formation of V_5Si_3, while V_3Si becomes more significant. Further increasing temperature to 990 °C leads to considerable increase in the amount of V_5Si_3 associated with continuous reduction of V peaks; the V_3Si peaks in this stage almost vanish. When the sample was finally heated to 1250 °C, most of the V_5Si_3 transformed to VSi_2 generating a significant exothermic peak as shown in Fig. 2(a).

Since the annealing treatment preferentially promotes formation of the V-richest intermetallic compounds, it is argued that silicon diffuses faster than vanadium. When Si content reaches a certain level, V crystal structure becomes unstable and transforms to the stable V-rich intermetallic compounds, such as V_3Si and V_5Si_3. The formation of VSi_2 in the subsequent annealing stage is governed by further Si diffusion into V_5Si_3 and V_3Si. It should be noted that, in MA2 and MA3 samples milled for 1 h, a large amount of V_5Si_3 still exists after heating to 1250 °C (see Fig. 4) suggesting that the addition of SiC and C strongly hinders diffusion of residual Si into the previously formed V-rich compounds.

The reasons for such a hindering effect are not yet completely clear. SiC in the MA2 system significantly speeds up SSRs during MA, but it delays the formation of VSi_2 in annealing. A tentative explanation is presented in the following. During MA, fresh interfaces, where SSRs take place, are continuously created by repeated fracturing and welding, so that long-distance atomic diffusion is not needed. On the contrary, in the case of annealing, SSRs occur first at the interfaces generated by MA, but further phase transformation requires longer-distance atomic transportation. In this situation, the presence of SiC can hinder atomic diffusion. In addition, considering the MA3 system, the competitive V–C and Si–C reactions occurring in the annealing process can delay VSi_2 formation.

Since it is generally accepted that in both MA and annealing processes the SSRs are promoted by similar mechanisms [19,20], it could be assumed that the fast diffusion of silicon also occurs in the MA process. The question should arise then why we are not able to ascertain the formation of V-rich phases during MA. The fact that the silicon might diffuse fast in both thermal and mechanical treatments does not ensure that the same intermediates are encountered in the two different processes. A similar behaviour has been already noticed in the Pd–Si [21] and Ni–Al [22] systems where the

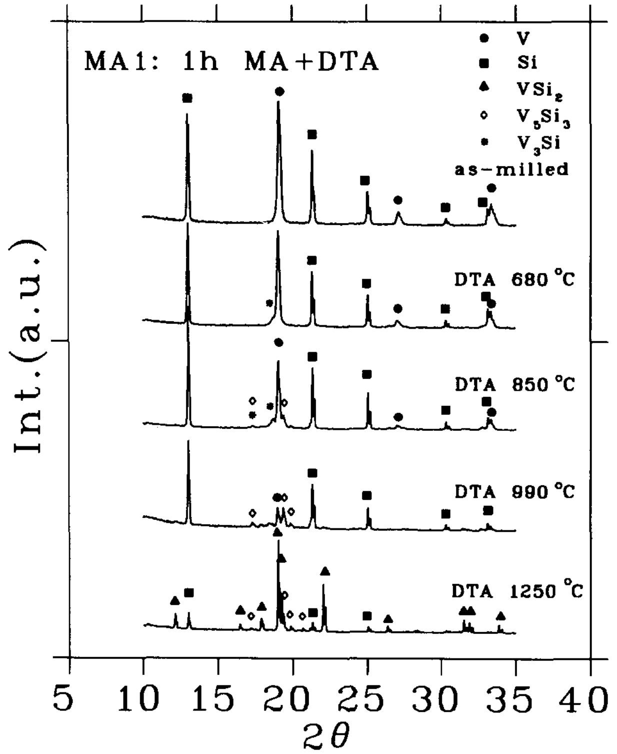

Fig. 5. XRD patterns of MA1 powder mixture milled for 1 h and treated by DTA at different temperatures.

first phase formed is different in MA and thermal treatment. Kinetic constraints and stability of the final equilibrium phase may be involved to explain this behaviour [21]. In addition, in the present case small amounts of V_3Si and V_5Si_3 formed during MA could probably be masked in the X-ray pattern by the broadening of the V(110) peak falling very close to the strongest reflections of the two V-rich silicides.

On the basis of the present results, however, it cannot be ultimately excluded that the phase formation mechanisms are really different in mechanical and thermal activation processes.

5. Conclusions

(1) Nanostructured intermetallic VSi_2 and a VSi_2–SiC composite have been successfully obtained by MA starting from elemental powders and elemental powders plus SiC.

(2) The presence of SiC (added or formed) considerably hampers grain growth of VSi_2 in the annealing process.

(3) The successful fabrication of a VSi_2–SiC composite in the present work should provide a hint for the preparation of other advanced intermetallic–ceramic composites by MA directly starting from the elements.

Acknowledgment

The author L. Liu undertook this work with the support of the ICTP programme for training and research in Italian laboratories at Trieste, Italy.

References

[1] J. Kajuch, J.D. Rigney and J.J. Lewandowski, *Mater. Sci. Eng. A, 155* (1992) 59.
[2] C.H. Henager, Jr., J.L. Brimhall and J.P. Hirth, *Mater. Sci. Eng. A, 155* (1992) 109.
[3] K. Sadananda, H. Jones, J. Feng, J.J. Petrovic and A.K. Vasudevan, *Ceram. Eng. Sci. Proc., 12* (1991) 1671.
[4] K.M. Aiken, Jr., *Ceram. Eng. Sci. Proc., 12* (1991) 1643.
[5] L. Xiao and R. Abbaschian, *Mater. Sci. Eng. A, 155* (1992) 135.
[6] J.J. Lewandowski, D. Dimiduk, W. Kerr and M.G. Mendiratta, *Mater. Res. Soc. Symp. Proc., 120* (1988) 103.
[7] F.D. Gac and J.J. Petrovic, *J. Am. Ceram. Soc. C, 68* (1985) 200.
[8] M.G. Mendiratta and D.M. Dimiduk, *Mater. Res. Soc. Symp. Proc., 133* (1989) 441.
[9] B. Aronsson, T. Lundstrom and S. Rundqvist, *Borides, Silicides and Phosphides*, Wiley, New York, 1965.
[10] M. Oehring and R. Bormann, *Mater. Sci. Eng. A, 134* (1991) 1330.
[11] B. Bokhonov, E. Ivanov and V. Boldyrev, *J. Alloys Comp., 199* (1993) 125.
[12] L. Liu and Y.D. Dong, *Nano-struct. Mater., 2* (1993) 463.
[13] N. Malhauroux-Gaffet and E. Gaffet, *J. Alloys Comp., 198* (1993) 143.
[14] R.B. Schwarz, S.R. Srinivasan, J.J. Petrovic and C.J. Maggiore, *Mater. Sci. Eng. A, 155* (1992) 75.
[15] L. Liu, F. Padella, W. Guo and M. Magini, *Acta Metall. Mater.*, in press.
[16] R.K. Viswanadham, S.K. Mannan and S. Kumar, *Scr. Metall., 22* (1988) 1011.
[17] F. Petoldt, B. Scholz and H.-D. Kunze, *Mater. Lett., 5* (1987) 280.
[18] C.C. Koch, *Annu. Rev. Mater. Sci., 19* (1989) 121.
[19] C. Politis and W.L. Johnson, *J. Appl. Phys., 60* (1986) 1147.
[20] B. Fultz, G. Lecaer and P. Matteazzi, *J. Mater. Sci., 4* (1989) 1250.
[21] F. Padella, E. Paradisco, N. Burgio, M. Magini, S. Martelli, W. Guo and A. Iasonna, *J. Less-Common Met., 175* (1991) 79.
[22] W. Guo, M. Magini, F. Padella, L. Battezzati, M. Baricco and F. Fracchia, *Int. J. Mechanochem. Mech. Alloy., 1* (1994) 97.