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Comparison of solid-state amorphization reactions in deformed Ni-Ti and Ni-Zr multilayered composites

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Differential scanning calorimetry and x-ray-diffraction analysis were utilized to compare solid-state reactions in multilayered composites of two different metal systems: Ni-Zr and Ni-Ti. We found that solid-state amorphization reactions occurred in both the Ni-Zr and the Ni-Ti system. Our results indicate that a suitable kinetic constraint exists on the formation of crystalline intermetallic compounds in the Ni-Ti system such that solid-state amorphization reactions can occur in this system, although the relatively sluggish growth of amorphous material in the Ni/Ti composites limits the thickness that can be grown. The differences between the kinetics of the solid-state amorphization reactions in these two systems provide some insight into the nature of the solid-state amorphization process.

I. INTRODUCTION

Single-phase amorphous alloys can form in diffusion couples at relatively low temperatures (approximately half the pertinent melting temperatures) by means of interdiffusion of pure, polycrystalline elements.[1–12] A number of requirements have been proposed for the formation of amorphous alloys in diffusion couples by means of solid-state reaction.[1,2,4] The two metals that form the diffusion couple must possess a large, negative heat of mixing in the amorphous phase in order to drive the reaction. There must be a dominant moving species; i.e., one constituent of the diffusion couple should exhibit a much greater mobility than the other.[4–6] The movement of both constituents is apparently required to nucleate and grow crystalline material, while the mobility of only one constituent is required to grow an amorphous alloy. Such a disparity in the mobility of the atoms in the diffusion couple provides a constraint on the formation of equilibrium intermetallic compounds in a given temperature range and time frame, i.e., a kinetic constraint. It has also been indicated that initially, in the as-prepared composite, a certain degree of disorder present at the interface between the polycrystalline metals (if not an amorphous interfacial region) facilitates the growth of amorphous material. Without such existent disorder at the interface, the nucleation and growth of equilibrium intermetallic compounds may be favored.[7,8]

The present study concerns a comparison of solid-state reactions in the Ni-Ti system and the Ni-Zr system. As both Zr and Ti are group-IVA elements, these systems are considered to be chemically and thermodynamically similar.[13] Solid-state amorphization reactions occur in both systems, but it is the differences between these solid-state amorphization reactions which reveal some information that may be relevant to an understanding of the micromechanisms of these reactions.

A consideration of some of the parameters for the Ni-Ti and Ni-Zr systems considered to be relevant to the success of solid-state amorphization reactions at the expense of the production of crystalline material reveals a number of similarities. Amorphous alloys can be produced by means of rapid quenching from the melt in both the Ni-Ti and the Ni-Zr systems over a wide range of compositions, ranging from roughly 30 to 70 at.% Ni.[14–19] These amorphous alloys are relatively stable, and generally exhibit similar crystallization temperatures, although Ni-Ti amorphous alloys show less thermal stability at high Ni concentrations, as seen in Fig. 1. The heats of formation of amorphous alloys in the Ni-Ti system are found to be similar to those of similar stoichiometry in the Ni-Zr system, with values of about 40 kJ/mole for stoichiometries with 60 at.% nickel.[14–16] Anomalously fast diffusion of Ni atoms is observed in both α-Ti and α-Zr, although Ni has been observed to diffuse one to two orders of magnitude faster in Zr than in Ti. The diffusion constant at a temperature of 971 K of Ni atoms in α-Ti was observed[25–27] to be 1.8×10^{-9} $\mathrm{cm}^2\,\mathrm{s}^{-1}$ and the diffusion constant at the same temperature of Ni in α-Zr was observed to be almost two orders of magnitude greater, $1.2\times10^{-7}\ \mathrm{cm}^2\,\mathrm{s}^{-1}$.

The difference in atomic volumes for Ni and Zr is significantly greater than for Ni and Ti. Clemens has observed some correlation between success in the formation of amorphous alloys by means of solid-state reaction in binary metal systems and differences in atomic volume of the constituents.[28] That is to say, based on this criteria alone, composites from the Ni-Zr system would be more likely to undergo solid-state amorphization reactions.

Despite the large number of similarities between the Ni-Ti and the Ni-Zr systems with regards to the parameters considered relevant to solid-state amorphization reactions, different results have been observed in these two systems. Solid-state reactions in a variety of multilayered Ni/Zr composites at temperatures below approximately 600 K produce an amorphous alloy.[2,10–12,28–33] For instance, a sputtered multilayered Ni/Zr diffusion couple with equal layer thicknesses of less than 1000 Å can be

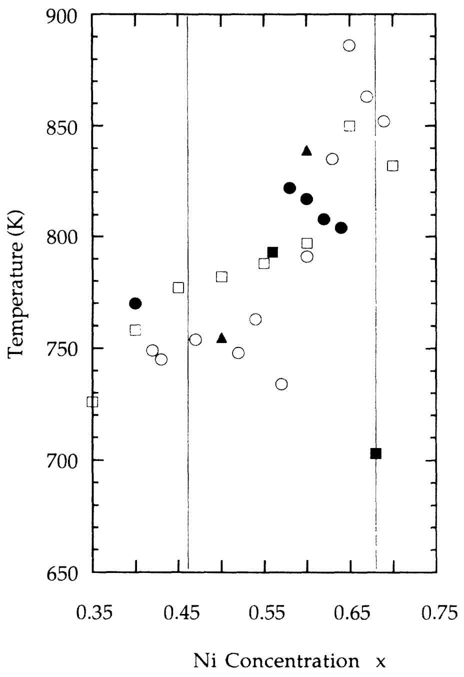

FIG. 1. A comparison of the crystallization temperatures at a constant heating rate on order of 20 K/min for rapidly quenched Ni-Ti and Ni-Zr metallic glasses as a function of Ni content. Solid symbols: Ni-Ti system. Open symbols: Ni-Zr system. ■: vapor deposited Ni-Ti, see Ref. 20. ●: liquid quenched Ni-Ti, see Ref. 18. ▲: ball-milled Ni-Ti, see Refs. 21–23. □: vapor deposited Ni-Zr, see Ref. 24. ○: liquid quenched Ni-Zr, see Ref. 19.

completely amorphized at temperatures less than 700 K.[10] Studies of solid-state reactions in multilayered composites in the Ni-Ti system indicate difficulty in producing amorphous material under similar annealing conditions.[13,31,32,34]

Clemens *et al.* have reported[31] that a certain degree of disorder at the interfaces was apparently required to grow the amorphous phase in Ni/Ti multilayered composites. The degree of order at the interfaces was controlled by either varying the thickness of the interlayers[28] or by controlling the sputtering pressure during atomic deposition,[31] and was characterized by means of x-ray diffraction in both reflection and transmission geometries. In a separate work, Meng *et al.* have indicated that heat treatments at temperatures less than 600 K of Ni-Ti composites produced by means of sputtering or by electron-beam evaporation result in the formation of the intermetallic compound $Ni_{50}Ti_{50}$ with a CsCl structure.[13] It was suggested[13] that the difference in the structures of the equilibrium compounds in the two systems results in distinctly different kinetics for the nucleation and growth of intermetallic compounds in the diffusion couple.

Numerous reports of the production of amorphous powders by means of a different technique, ball milling, have been made for both the Ni-Ti and the Ni-Zr systems. One would expect a large degree of disorder in the ball-milled particles, and thus at the interfaces in ball-milled binary mechanical mixtures, as has been pointed out previously by a number of investigators.[23,24,35–39]

In the present work we seek to investigate the difference in the reaction kinetics in these two systems by means of differential scanning calorimetry (DSC) measurements[33] on mechanically deformed,[40] multilayered composites of Ni/Zr and Ni/Ti. We have determined that a similar kinetic constraint exists on the formation of crystalline intermetallic compounds in both the Ni-Ti and the Ni-Zr systems. The growth of amorphous material in our Ni/Ti composites is apparently facilitated by the relatively large degree of disorder induced in the metal layers, and therefore at the interfaces, by the mechanical-deformation process. We find that the growth of amorphous material is significantly slower in the Ni-Ti system than in the Ni-Zr system. This difference in growth rates limits the amount of amorphous material that can be grown by means of solid-state amorphization reactions in the Ni-Ti system.

II. EXPERIMENT

Samples utilized for study are composites of multilayered metals, with individual layer thicknesses varied in different samples from ≈100 to 20 000 Å. Bulk composites are prepared by means of mechanical deformation in a rolling mill. The mill had two parallel rolls each of radius 4.3 cm, and was operated at 21 rpm with minimal lubrication on the rolls. Multilayered composites of both Ni/Zr and Ni/Ti with similar geometries and degrees of deformation were prepared by means of mechanical deformation. Zr and Ti foils were prepared to be of similar thicknesses. Identical foils of Ni were folded with the foils of either Zr or Ti. The composites were placed in rectangular stainless-steel sheaths for deformation in the rolling mill. The initial thickness of the composite was generally on the order of 50 μm. It was observed that upon rolling the thickness of the foils decreased, the length increased while the width remained essentially constant. Initially, before foils bonded together to make a composite, the Ni rolled at a slightly higher rate than either Zr or Ti. It was observed that in the described process Zr and Ti deformed in a similar fashion and that the Zr and Ni, or Ti and Ni, foils cold welded together to form a composite, with no apparent adhesion to the stainless-steel sheath. The increase in length of the composite matched the increase in length of the stainless-steel sheath; qualitative observation indicated that the mechanical properties of the stainless steel dominated the deformation behavior of the composite-sheath configuration. The composite was removed from the deformed stainless steel and the procedure was then repeated (with the deformed sample folded over on itself) a number of times depending on the desired sample configuration (degree of deformation and the thickness of individual layers). Identical rolling conditions were imposed on both Ni/Ti and Ni/Zr composites, and it was indicated that the composites deformed under these conditions in a similar fashion. For instance, thicknesses of both types of composites were the same and uniform to within ≈3 μm after similar rolling treatments.

The foils utilized in this study were purchased commercially from several sources, or were obtained by cold-rolling ingots. The degree of deformation of a composite was characterized with the reduction ratio, $R=(i/f)2^n$, with the initial thickness i and final thickness f of the composite, and n the number of times the composite is folded over on itself between runs. The reduction ratio provides a qualitative indication of the individual layer thicknesses and of the total interfacial area between individual layers, where ideally, for a given composite, individual layer thickness varies inversely with R and the surface area is proportional to R. In practice there is a distribution of layer thicknesses and R is a qualitative indication of the composite configuration. The reduction of individual layer thicknesses slows with increasing deformation, so that the interfacial surface area increases much more slowly than the reduction ratio R.

The structures and phases of the samples in the as-prepared state as well as at various degrees of reaction are characterized by means of x-ray-diffraction analysis and electron microscopy. Both Ni/Ti and Ni/Zr composites of $R=100$ and 1000 were examined by means of scanning electron microscopy in order to characterize and compare the individual layer thicknesses in both systems. At a given reduction ratio, similar layer thicknesses were observed in composites in both systems. Ni/Ti composites were examined most extensively and were found to exhibit layered structures similar to those previously observed[40] by means of scanning electron microscopy in Ni/Zr composites produced by means of rolling, with similar layer thicknesses at similar reduction ratios. Thus it was concluded that layered composites could be produced in both systems with similar geometries, with average layer thicknesses the same within a factor of 2. The average layer thicknesses in these composites of reduction ratio $R=100$ was found to be 4000 Å, while composites of reduction ratio $R=1000$ exhibited average layer thicknesses of 1700 Å.

Samples were examined by means of x-ray diffraction in both the as-prepared state and after heat treatment. For transmission electron microscopy work some regions of some samples were also examined in the as-prepared state. These samples were rolled to bulk thicknesses of a few micrometers such that holes developed in the samples. The regions near these holes could be examined by means of transmission electron microscopy. Thicker regions were ion milled to thicknesses thin enough to allow the passage of electrons at 125 keV. Similar results were observed for both sample preparation techniques in this study. A Rigaku x-ray diffractometer with Ni-filtered, Cu K_α radiation was utilized to obtain x-ray-diffraction profiles of samples, while a Hitachi 7000 transmission electron microscope operated at 125 keV was utilized to obtain selected area diffraction profiles for samples.

Reactions in diffusion couples of the Ni-Ti system or the Ni-Zr system are initiated as the samples (hermetically sealed in aluminum pans) are heated at a constant rate above room temperature in the DSC.[10,33] The rate of heat release is measured by means of DSC through the course of a reaction. Each DSC scan was followed by a second scan (identical thermal conditions) of the sample; the data from the second scan were subtracted from the data of the first scan. A Perkin-Elmer DSC-4 interfaced to a Compaq Deskpro 286 computer was utilized for DSC measurements.

III. RESULTS AND DISCUSSION

A comparison of solid-state reactions by means of DSC indicates that at lower temperatures the solid-state reaction in the Ni/Zr composite is significantly faster than the solid-state reaction in the Ni/Ti composite. This comparison also reveals a discontinuous dependence of the reactions in the Ni/Ti samples on the degree of deformation, in contrast with observations of the Ni/Zr system. The growth of amorphous material in our Ni/Ti composites is apparently facilitated by the relatively large degree of disorder induced in the metal layers, and therefore at the interfaces, by the mechanical deformation process.

A series of DSC thermograms of Zr-Ni multilayer composites all of average stoichiometry $Ni_{22}Zr_{78}$ mechanically deformed to various degrees (reduction ratios from 130 to 8600) are displayed in Fig. 2. Upon heating Ni/Zr multilayered composites (e.g., samples similar to those utilized to produce the data in Fig. 2) at constant rates near 20 K/min to temperatures below approximately 620 K, quenching to 320 K, and performing x-ray analysis, a broad peak associated with amorphous material along with sharp Bragg peaks associated with unreacted Ni and Zr are observed.[33,41] Repeating this procedure with heating to temperatures above about 650 K generally results

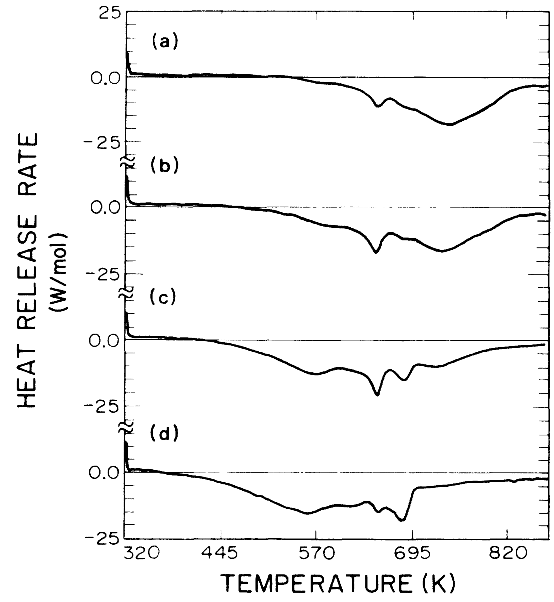

FIG. 2. The heat-flow rate as a function of temperature for a constant scan rate of 20 K/min, measured by means of differential scanning calorimetry. The samples were multilayered composites of average stoichiometry $Ni_{22}Zr_{78}$ produced by codeformation of the two metals. The initial thicknesses were the same for all samples, while the degree of deformation varied. The degree of deformation of each composite is reflected in the reduction ratio. The data are for reduction ratios of (a) 130, (b) 260, (c) 1100, and (d) 8600.

in the observation of additional Bragg peaks associated with intermetallic compounds. Both DSC and x-ray-diffraction data indicate that as the sample is deformed and the average layer thickness decreases (i.e., the interfacial area increases), an increasing fraction of the sample reacts at temperatures below 620 K. In fact, an examination of the dependence of the integrated heat release below 620 K on the estimated interfacial area for the DSC data of Fig. 2 reveals a linear relation. This observation that the amount of amorphous material formed at low temperatures is proportional to the interfacial area agrees with previous, more precise observations.[10-12]

In the Ni/Ti system we are able to observe formation of amorphous material by solid-state reaction only in composites with a rather high degree of deformation (a reduction ratio greater than ≈ 350), and this reaction is relatively slow. A series of DSC thermograms of Ni-Ti multilayer composites all of average stoichiometry $Ni_{50}Ti_{50}$ mechanically deformed to various degrees (reduction ratios from 40 to 1050) are presented in Fig. 3. The reaction rate below 620 K is negligible or very small for the samples of reduction ratio less than or equal to 300, in marked contrast to samples of similar geometry in the Ni-Zr system [Figs. 2(a) and 2(b)], where a significant fraction of the sample has already formed amorphous material [e.g., approximately 25% for a sample of reduction ratio 260, Fig. 2(b)]. For the Ni-Ti sample of reduction ratio 1050 [Fig. 3(d)], a reaction rate is first observed at temperatures below 500 K and a fraction of the sample (on order 10%) has reacted at temperatures below 620 K, significantly less than the corresponding sample in the Ni-Zr system [Fig. 2(c)].

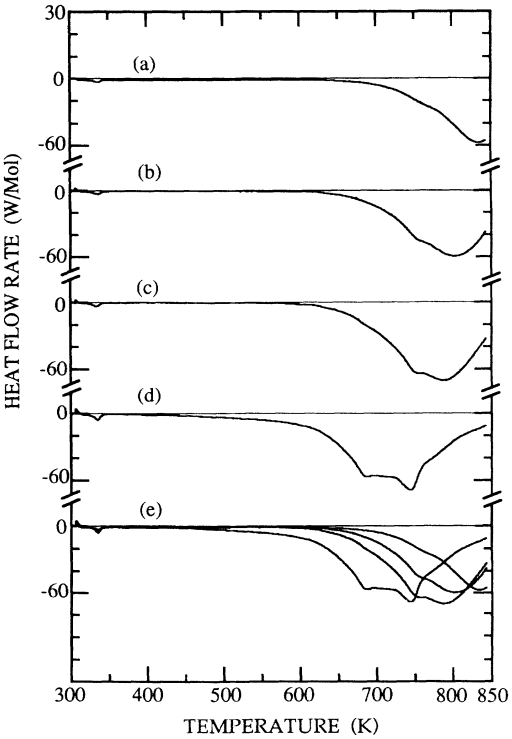

FIG. 3. The heat-flow rate as a function of temperature for a constant scan rate of 20 K/min, measured by means of differential scanning calorimetry. The samples were multilayered composites of average stoichiometry $Ni_{50}Ti_{50}$ produced by codeformation of the two metals. The initial thicknesses were the same for all samples, while the degree of deformation varied. The degree of deformation of each composite is reflected in the reduction ratio. The data are for reduction ratios of (a) 40, (b) 120, (c) 300, and (d) 1050. (e) represents the data of parts (a)–(d) on the same graph.

The amount of sample reacted at low temperatures in the Ni/Ti system is not proportional to the interfacial area in the sample, in marked contrast with the Ni-Zr system. We estimate that the interfacial area increases by about a factor of 1.5 with an increase of reduction ratio from 300 to 1050, whereas the integrated heat release at low temperature (below 630 K) increases by a factor of approximately 40. Furthermore, in the Ni-Ti system, only the DSC trace [Fig. 3(d)] for the sample with the greatest degree of deformation shows a distinct peak at 680 K (an indication of such a peak may be visible in the DSC curve for the sample of reduction ratio 300). The shape of the DSC curve following this peak is distinctly different than the DSC curves of lower reduction ratio. The implication is that a different reaction is occurring in the more highly deformed sample. This result is consistent with previous observation that in the production of amorphous Ni-Ti by means of ball milling, the formation of amorphous material was only observed after prolonged milling, i.e., at high deformation.[23,35,38] This result is also consistent with the observation that a certain degree of disorder was necessary to facilitate solid-state amorphization reactions in Ni/Ti thin-film multilayered composites.

Upon heating samples similar to those utilized to produce the data in Fig. 3 to temperatures below 600 K, quenching to 320 K, and performing x-ray analysis, Bragg peaks associated with unreacted Ni and Ti are observed for the samples of reduction ratio less than 350 (Fig. 4). X-ray analysis of more highly deformed Ni/Ti composites (i.e., reduction ratio greater than 1000) heated to temperatures between 630 and 660 K and rapidly cooled to room temperature reveal Bragg peaks corresponding to the elements Ni and Ti, and a broad peak centered at $2\theta \approx 43.5°$ [e.g., Fig. 4(b)]. Such a broad peak in x-ray scans is indicative of amorphous material,[18,34,38] and the angle of its maximum corresponds to that of liquid quenched metallic glass of composition near $Ni_{63}Ti_{37}$. X-ray analysis of similar samples heated to temperatures of 670 K and rapidly cooled to room temperature reveal Bragg peaks corresponding to the elements, Ni and Ti, and new small Bragg peaks corresponding to either the intermetallic compound $Ni_{50}Ti_{50}$ or to the intermetallic compound Ni_3Ti, indicating that a small amount of crystalline material has been formed[35,42] [Fig. 4(c)]. Upon examining numerous such Ni/Ti composites utilizing DSC and x-ray analysis we are able to correlate such a distinct change in the kinetics of the solid-state reaction (as evidenced by a peak at a temperature near 660 K in DSC scans at a constant heating rate of 20 K/min) with an indication by means of x-ray analysis of the presence of a small amount of crystalline material in the sample.

Similar specimens examined in plane-view geometry with a Hitachi 7000 transmission electron microscope operated at 125 keV provide selected area diffraction patterns which indicate the same correlations between heat treatments, i.e., the formation of the amorphous phase upon heating followed by crystalline material at slightly higher temperature. In Fig. 5 we observe distinct differences between transmission electron microscope selected area diffraction profiles for similar samples heated at identical heating rates to slightly different temperatures, 660 and 670 K. Upon heating to 660 K and rapidly cooling to room temperature, selected area diffraction reveals Bragg rings corresponding to Ni and Ti with a diffuse ring indicative of amorphous material of stoichiometry near $Ni_{60}Ti_{40}$. In some cases there is in these electron-diffraction patterns an indication of a weak, partial ring most likely corresponding to the initial formation of the intermetallic compound Ni_3Ti. Similar samples heated to a slightly higher temperature, 670 K, and rapidly cooled to room temperature, show no trace of the diffuse ring, but instead reveal a number of new Bragg rings corresponding to Ni_3Ti and NiTi. These data agree with observations by means of x-ray diffraction; we are able to correlate a distinct change in the kinetics of the solid-state reaction with the appearance of intermetallic compounds in the sample.

We have observed the growth in our mechanically deformed Ni/Ti composites at low temperatures of what appears to be an amorphous alloy. In the absence of a complete transformation of a sample to the amorphous

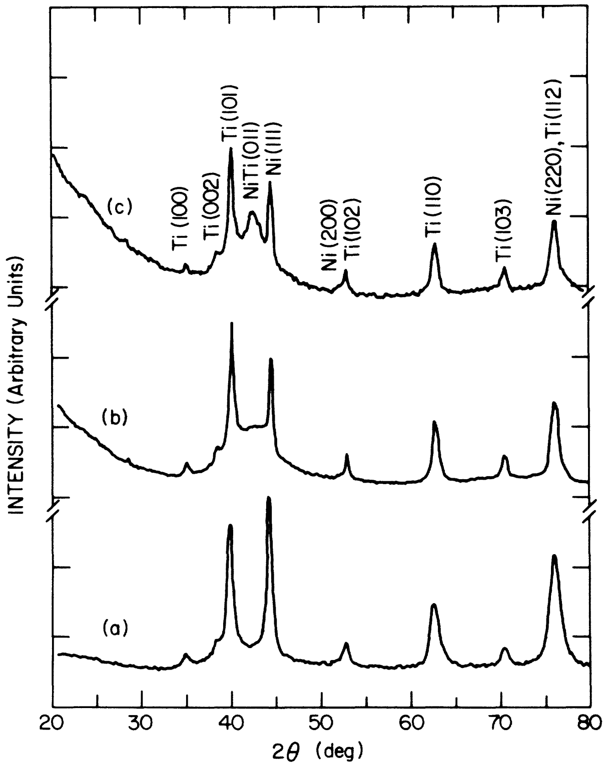

FIG. 4. X-ray diffraction profiles (Cu K_α radiation) for a multilayered composite of Ni and Ti of average stoichiometry $Ni_{50}Ti_{50}$ and reduction ratio of 10^4. (a) The as-codeformed sample. (b) The sample after being heated at 10 K/min to a temperature of 658 K and quenched to room temperature in the differential scanning calorimeter. (c) The sample after being heated at 10 K/min to a temperature of 668 K and quenched to room temperature in the differential scanning calorimeter.

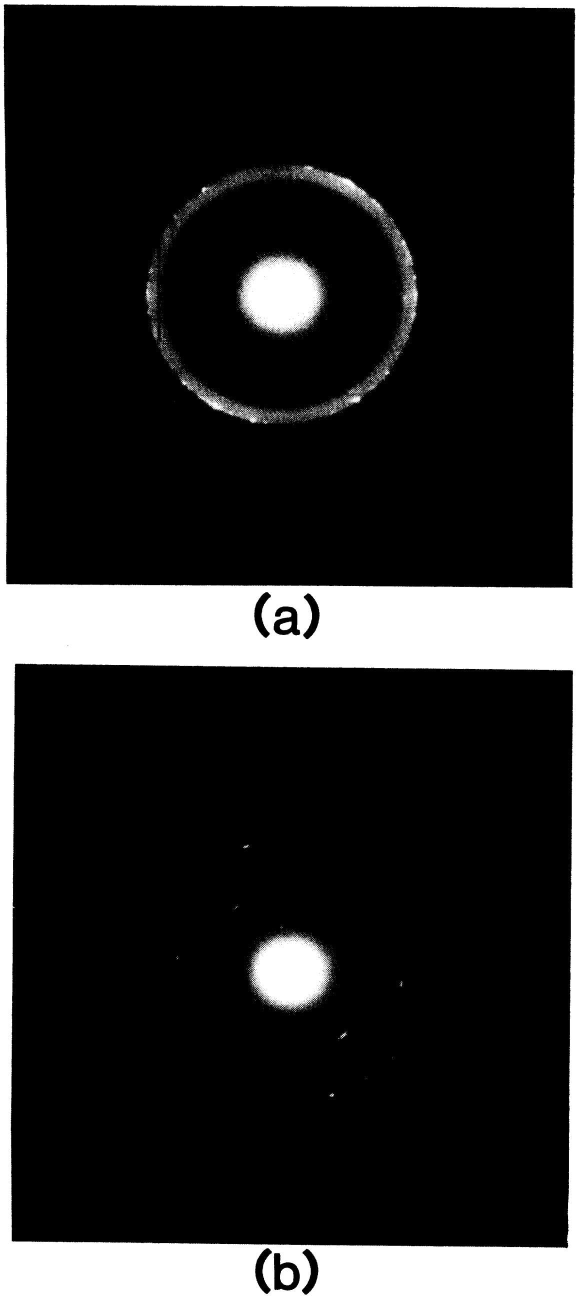

FIG. 5. Selected area diffraction patterns for a multilayered composite of Ni and Ti of average stoichiometry $Ni_{50}Ti_{50}$. Samples were examined in plane-view geometry with an electron microscope operated at 125 keV. (a) The sample after being heated at 10 K/min to a temperature of 670 K and rapidly cooled to room temperature in the differential scanning calorimeter. (b) A similar sample after being heated at 10 K/min to a temperature of 670 K and rapidly cooled to room temperature in the differential scanning calorimeter.

phase, our identification of the new phase as amorphous is not definite. A nanocrystalline material would yield similar diffraction patterns, but the thermal (DSC) data are inconsistent with a continuous grain growth process. That is to say, if a nanocrystalline equilibrium compound were forming at temperatures below 660 K, we would expect these small grains to grow in a continuous fashion at higher temperatures, rather than to disappear. The distinct change in the DSC traces near 650 K are consistent with a nucleation process. Such a signal correlated with the disappearance of the diffraction signature of amorphous material and the appearance of evidence of intermetallic phases within a short time and temperature span strongly suggest the crystallization of a growing amorphous phase.[43,44]

After heating deformed multilayered composites of average stoichiometry $Ni_{48}Ti_{52}$ and R of 1500 to a higher temperature of about 750 K, an additional peak is observed in DSC scans of these Ni/Ti composites [e.g., Fig. 3(d)]. This peak is correlated by means of x-ray diffraction with the formation of the intermetallic compound $NiTi_2$. An x-ray-diffraction profile of a similar sample heated to a temperature of 730 K and cooled rapidly to room temperature reveals Bragg peaks corresponding to the intermetallic compounds Ni_3Ti and NiTi [Fig. 6(a)], while higher quench temperatures of 755 and 780 K result in x-ray-diffraction profiles with Bragg peaks corresponding to $NiTi_2$ [see Figs. 6(b) and 6(c)]. The correlated thermal event is distinctly separate from the thermal events described previously for this system, and occurs after all the amorphous material has crystallized. Thus it is implied that $NiTi_2$ is formed at the interface between the intermetallic compound NiTi and crystalline Ti.[42] These observations provide some indication that the composition gradient in the growing amorphous phase is bounded by an endpoint of stoichiometry near equiatomic amorphous NiTi. If this were not the case, one would expect that the crystallization of the growing amorphous phase would result in the formation of some $NiTi_2$ at a much lower temperature, analogous to the formation of both intermetallic compounds NiTi and $NiTi_2$ upon the crystallization of liquid quenched metallic glass of stoichiometry $Ni_{40}Ti_{60}$.[18]

The DSC scans of Fig. 7 for composites of various stoichiometries also indicate that upon heating highly deformed Ni/Ti composites at a constant rate from room

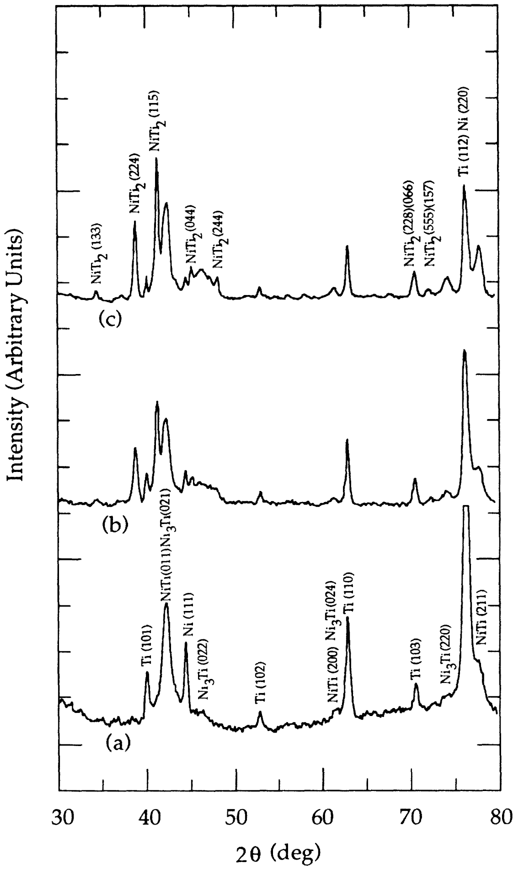

FIG. 6. X-ray-diffraction profiles (Cu K_α radiation) for a multilayered composite of Ni and Ti of average stoichiometry $Ni_{48}Ti_{52}$. (a) The sample after being heated at 20 K/min to a temperature of 730 K and quenched to room temperature in the differential scanning calorimeter. (b) The sample after being heated at 10 K/min to a temperature of 755 K and quenched to room temperature in the differential scanning calorimeter. (c) The sample after being heated at 10 K/min to a temperature of 780 K and quenched to room temperature in the differential scanning calorimeter.

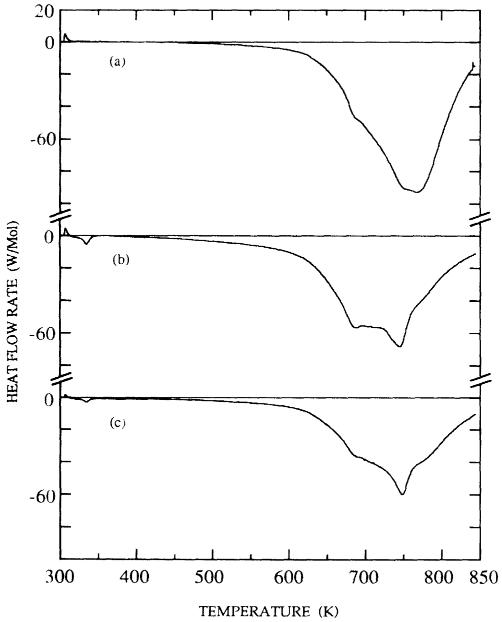

FIG. 7. The heat-flow rate as a function of temperature for a constant scan rate of 20 K/min, measured by means of differential scanning calorimetry. The samples were multilayered composites of three different stoichiometries produced by codeformation of the two metals. The degree of deformation was the same for all samples, while the initial thicknesses of the Ni and Ti foils were varied to provide different average stoichiometries. (a) An average stoichiometry of Ni_3Ti, (b) an average stoichiometry of $Ni_{50}Ti_{50}$, and (c) an average stoichiometry of $NiTi_2$.

temperature to high temperatures, a solid-state amorphization reaction ensues, followed by the nucleation and growth of crystalline compounds. The intermetallic compounds Ni_3Ti and $Ni_{50}Ti_{50}$ form first, apparently at similar temperatures, with the intermetallic compound $NiTi_2$ forming at distinctly higher temperature. X-ray-diffraction profiles of samples heated to various temperatures and cooled rapidly to room temperature indicate that Ni_3Ti grows more slowly than NiTi. This observation is consistent with previous observations of interdiffusion at much higher temperatures and longer times (e.g., temperatures between 800 and 1200 K and annealing times on the order of 100 h).[42]

We examine (Fig. 7) the dependence of solid-state reaction in Ni/Ti composites on the average stoichiometry of the composite (i.e., on the relative thicknesses of the layers of the composite). As samples are heated at a constant rate from room temperature, it is observed that for temperatures below 700 K the reactions are similar for Ni/Ti composites of all average stoichiometries. At higher temperatures, the solid-state reactions for these composites reveal a dependence on average sample stoichiometry. For instance, we observe by means of differential scanning calorimetry [Fig. 7(a)] a higher rate of heat release at temperatures above 700 K for Ni-rich, Ni/Ti multilayered composites than for other stoichiometries. Apparently Ni_3Ti is being formed, and the higher rate of heat release during this reaction reflects in part the higher enthalpy of formation of this compound, Ni_3Ti, as compared to other equilibrium compounds which form at these high temperatures.[16] The progress of the solid-state reactions at higher temperatures apparently reflects the relative abundance (i.e., the thicknesses of the layers) of crystalline Ni and crystalline Ti as the supply of one of these materials is exhausted.[41]

The initial growth of an amorphous phase at the Ni/Ti interface followed by crystallization at higher temperatures are similar to phenomena in the Ni-Zr system. It is of interest that in Ni/Zr composites the formation of orthorhombic NiZr at the Zr interface alone can be isolated over a rather broad time span and temperature range.[13,44] This intermetallic compound was shown to coexist in the Ni/Zr multilayers with amorphous material richer in Ni content. In contrast, our experimental observations indicate that in the Ni/Ti system upon heating multilayered composites at a constant rate (on the order of 20 K/min), essentially the entire amorphous interlayer crystallizes within a small temperature interval on the order of 20 K. This observation may be related to the relative thickness of the amorphous interlayers in these two systems, and to the thermal stability of the amorphous material formed in the amorphous interlayers in these two systems.

The composition range across the growing amorphous layer in Ni-Zr diffusion couples during solid-state amorphization reactions has been estimated to extend from approximately 46 to 68 at.% Ni.[41,45] Because of the similarities of the thermodynamic properties of these systems, we would expect that the Ni-Ti system would exhibit similar concentration ranges in the growing amorphous phase. Some support for such an assumption is provided by the observation that the crystallization products observed with the initial crystallization of the growing amorphous phase are the intermetallic compounds NiTi and Ni_3Ti.

Previous study has shown that the crystallization temperatures of liquid quenched metallic glasses in the Ni-Zr system increase as the Ni content increases from about 40 to about 70 at.% (see Fig. 1). Therefore, the most Zr-rich amorphous material in the growing diffusion couple, which is in fact in contact with crystalline Zr, would be expected to be the least thermally stable in the Ni-Zr system. If we assume that a heterogeneous crystallization process can occur, the amorphous material at that interface may in fact be less stable than rapidly quenched metallic glass of similar stoichiometry. In fact, it has been observed that in amorphous Ni/Zr diffusion couples, crystallization occurs first at the Zr interface, while amorphous material richer in Ni content remains in the amorphous phase.[41,44] Orthorhombic NiZr is formed at the Zr interface and grows into the Zr metal, while the more Ni-rich amorphous material does not crystallize until higher temperature or longer anneal times.

In the NiTi system, a steady increase in thermal stability with increasing Ni content is not observed for liquid quenched metallic glasses (see Fig. 1). In fact, liquid quenched metallic glass of stoichiometry near $Ni_{70}Ti_{30}$ exhibits slightly lower crystallization temperatures than metallic glass of stoichiometry near $Ni_{45}Ti_{55}$, the expected approximate composition near the other end of the amorphous diffusion couple. Thus, if we assume similar thermal stabilities for amorphous material produced by means of solid-state reaction in an amorphous diffusion couple as for liquid quenched metallic glasses, there is an indication that the amorphous Ni-Ti phases which contact either crystalline Ni or Ti in the Ni/Ti diffusion couples would crystallize at similar temperatures (such a development also tacitly assumes that any heterogeneous crystallization processes for Ni-rich amorphous material in contact with Ni is similar to heterogeneous crystallization processes for Ti-rich amorphous material in contact with Ti). Rapid crystallization of the growing amorphous phase due to the similarity of the crystallization temperatures for the two endpoint concentrations may be exacerbated by the relatively small thicknesses of the slowly growing amorphous diffusion couples in the Ni/Ti system.

The results of DSC measurements at different heating rates on numerous Ni/Ti composites indicate that the kinetics of the initial formation of equilibrium compounds[41] are qualitatively similar in both the Ni/Zr and the Ni/Ti codeformed, multilayered composites. It is only at approximately 650 K (in DSC scans at 20 K/min) that crystalline intermetallic compounds are observed to grow in both the Ni-Ti and Ni-Zr systems. For our mechanically deformed Ni/Ti composite, we observe that upon increasing the heating rate of the composite in DSC scans, the peak in the observed heat-flow rate which has been correlated with the initial crystallization of the growing amorphous phase occurs at progressively higher temperatures (as shown in Fig. 8). This provides some indication that the crystallization process is thermally activated.

The initial formation of crystalline material in a growing amorphous phase in contact with elemental metals in a diffusion couple can be a relatively complex process. One analysis concludes that at a given temperature, the nucleation of crystalline material at a moving amorphous-crystalline interface occurs at a rate equal to or less than the rate for that same interface when stationary.[46,47] The rate for the nucleation of a crystalline nucleus at a stationary amorphous-interlayer–crystalline-element interface is estimated as

$$R = K\nu \exp[-(\Delta G^* + Q)/kT] = R_0 \exp(-E/kT) , \quad (1)$$

where K is a dimensionless constant, ν is an attempt frequency, Q is an activation energy for atomic transport in the interface region, and ΔG^* is a heterogeneous nucleation barrer.[46–49] The activation energy $E = \Delta G^* + Q$ and the rate constant R_0 can be utilized to cast this nucleation-rate expression in a standard form.

Considering the Ni-Zr system, it has been experimentally indicated that the amorphous-alloy–crystalline-Zr interface moves while the amorphous-alloy–crystalline-Ni interface remains essentially stationary, with respect to the Zr lattice.[5,6] Nevertheless, the initial nucleation and growth of crystalline material is observed at the moving interface. Apparently the relative stability of Ni-rich amorphous alloys as compared with Zr-rich amorphous alloys (see Fig. 1) is the dominant factor here, as opposed to interface velocity. Evidence does exist that structural relaxation decreases the averaged interdiffusion constant in the growing amorphous phase, thus decreasing the velocity of the moving interface in this system.[33]

If we assume that the growth of the amorphous interlayer is in fact too slow to hinder the nucleation process when a temperature is reached during a DSC scan such that rate of nucleation as predicted by Eq. (1) is appreciable, then we can proceed with a standard Kissinger analysis. The actual rate of formation of nuclei will depend on the fraction γ of the amorphous material at the interface which has crystallized through the function $f(\gamma)$. In the simplest of cases $f(\gamma) = (1-\gamma)$. That is,

$$d\gamma/dt = B(1-\gamma)\exp(-E/kT) , \quad (2)$$

where B is the new rate constant incorporating the total amount of interfacial area. We assume the rate of heat release corresponds to the rate of reaction:

$$d\gamma/dt \propto dH/dt , \quad (3)$$

so that we can monitor the crystallization by means of DSC. Equation (2) is consistent with the form of reaction assumed by Kissinger in his analysis of reaction-rate kinetics.[49]

On this basis a Kissinger analysis[49] was performed upon data gathered over a relatively wide range from DSC scans on the Ni-Zr system.[33] The resulting analysis indicates an activation energy for this process of 2.0±0.1 eV. A similar analysis can be attempted for DSC scans for composites from the NiTi system. In this case the crystallization peak is not as clearly defined. The analysis indicates that the activation energy for the formation and growth of crystalline material in the growing amorphous phase is 2.5 eV (see Figs. 8 and 9). It is difficult to estimate the error in the case of the Ni/Ti system, and although we believe this error to be appreciable, we interpret the results as an indication of similar kinetics for the initial crystallization of the growing amorphous phase. It is of interest that both these systems reveal, within the Kissinger analysis, constant kinetics for nucleation and growth of crystalline material in the growing amorphous phase.

Previous experiment[25,26] at temperatures near 1000 K has indicated that Ni atoms diffuse two orders of magnitude more rapidly in α-Zr than in α-Ti. We estimate the relative rate of interdiffusion in amorphous Ni/Ti diffusion couples as compared to that in amorphous Ni/Zr diffusion couples from our DSC measurements.[10–12] We assume that the growth of amorphous material is one-dimensional and diffusion controlled, and that the growing amorphous interlayer exhibits a linear concentration profile with constant interfacial compositions.[45] Then the following relationship[50] holds between the interlayer thickness X, the growth rate dX/dt, and the averaged interdiffusion coefficient D:

$$X\frac{dX}{dt} = \frac{\Delta c D}{x(1-x)} , \quad (4)$$

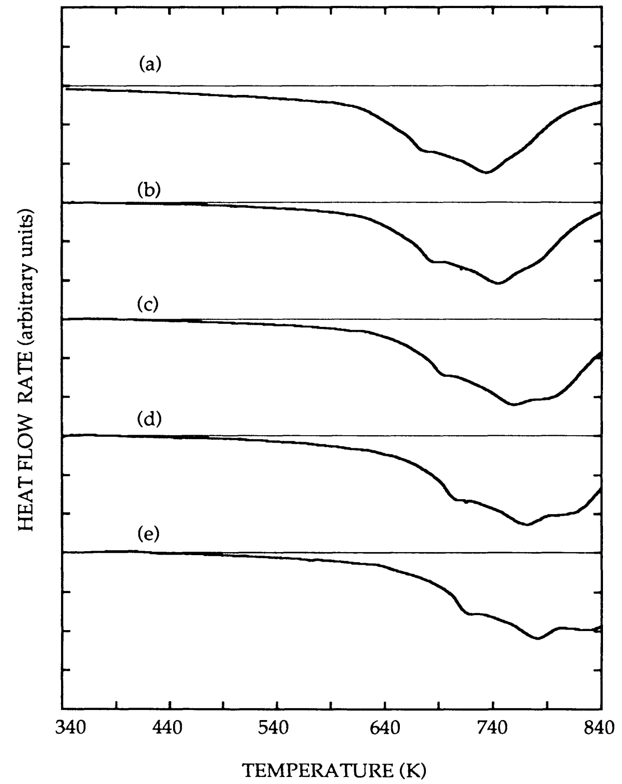

FIG. 8. The heat-flow rate as a function of temperature for mechanically deformed multilayered composites of Ni and Ti as measured by means of differential scanning calorimetry. The samples are all of average stoichiometry $Ni_{50}Ti_{50}$. The heating rates s for the differential scanning calorimetry scans were (a) 10 K/min, (b) 20 K/min, (c) 40 K/min, (d) 80 K/min, and (e) 160 K/min.

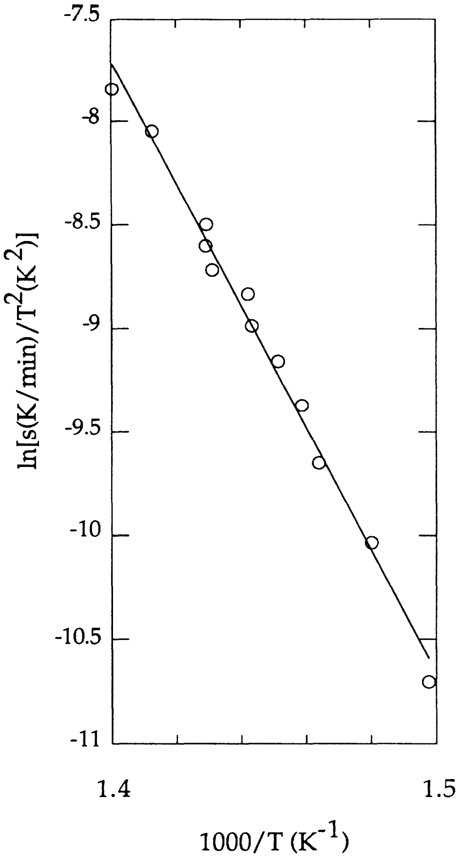

FIG. 9. The natural logarithm of the heating rate s divided by the square of the crystallization temperature T_c vs the inverse crystallization temperature. The solid line is a least-squares fit to the data (see caption for Fig. 8).

where Δc is the steady-state composition difference across the growing amorphous layer of average composition $\mathrm{Ni}_x\mathrm{Zr}_{1-x}$, and the ratio $\Delta c/[x(1-x)]$ is close to 1 for both our systems. With H_f the enthalpy of formation of an amorphous alloy at the average composition of the growing amorphous layer, we can quantify the proportionality[10–12] between the rate of heat release as measured by the DSC, dH/dt, and the rate of growth of the amorphous layer, dX/dt:

$$\frac{dH}{dt}=\frac{A\rho H_f}{M}\frac{dX}{dt}=b\frac{dX}{dt} , \tag{5}$$

where A is the total interfacial area of the composite, ρ is the average density, and M the molar mass of an amorphous alloy at the average composition of the growing amorphous layer, and the proportionality constant $b=(A\rho H_f/M)$. Using Eqs. (4) and (5) we obtain

$$H\,dH/dt \propto D , \tag{6}$$

where H is the integral of dH/dT from the initial reaction temperature to temperature T, and the proportionality constants (b) for the Ni-Ti and Ni-Zr systems for samples of equal interfacial area A are found to be the same within error of about 10%. Therefore our DSC data for samples with equal values of A (e.g., Figs. 2 and 3) reflect the relative rates of growth in these two systems, and a simple analysis of our data (including the DSC data in Fig. 3) on the basis of Eq. (6) provides an estimate of the relative rates of interdiffusion in the Ni-Ti and Ni-Zr systems. We find that at temperatures near 600 K, diffusion is more than an order of magnitude faster in the growing amorphous phase in the Ni-Zr system than in the Ni-Ti system, while a larger disparity is indicated at lower temperatures. At a temperature of 620 K we calculate the averaged interdiffusion coefficient in the growing amorphous Ni-Ti phase to be $D=10^{-14}$ cm^2/s.

The observed difference in growth rates in the Ni/Zr composites and the Ni/Ti composites appears to severely limit the amount of amorphous material that can be grown by means of solid-state amorphization reactions in the Ni-Ti system. A comparison of our calculated diffusion constants indicates that at a temperature of 580 K, the averaged interdiffusion constant in the growing amorphous phase is 20 times higher in Ni/Zr diffusion couples than in Ni/Ti diffusion couples. Our estimate of the maximum thicknesses of amorphous material which can be grown in our Ni/Ti composites before the formation of equilibrium compounds is less than about 100 Å, an order of magnitude smaller than the limiting thickness (1000 Å) experimentally observed in Ni/Zr composites.

The relatively small thickness of amorphous material which can be grown by solid-state reaction in the Ni-Ti system, combined with the indication that a disordered interface such as that produced by mechanical deformation facilitates these reactions, may provide some explanation for the relatively high degree of success experienced in the production of amorphous Ni-Ti by means of ball milling. Mechanically deforming powders by means of ball milling would most probably produce disordered interfaces. As previously noted,[23,24,35–39] the continual creation of new Ni/Ti interfaces, and the relatively low temperatures produced in the ball mill, allows for short diffusion distances. Thus, solid-state amorphization reactions may run under these conditions, while being frustrated in a more ordered geometry with an interlayer thickness on the order of 100 Å.

IV. CONCLUSIONS

We have investigated solid-state reactions in mechanically deformed composites in both the Ni-Ti and Ni-Zr systems. We find that, upon heating these composites from room temperature at a constant rate, amorphous material is the first phase to grow in both systems. Amorphous material grows one to two orders of magnitude more slowly in Ni/Ti composites than in Ni/Zr composites, in the temperature range of interest (500–650 K). We find that the intermetallic compounds form at essentially the same rate in both systems, i.e., that similar kinetic constraints on the formation of equilibrium compounds exist in both the Ni-Ti and Ni-Zr systems. The maximum thickness of amorphous Ni-Ti layers that were successfully grown was determined to be on order of 100 Å, an order of magnitude smaller than that observed for Ni/Zr diffusion couples, and appears to reflect the difference in mobilities of Ni in these two systems. We conclude that it is a smaller mobility of Ni in the growing amorphous Ni-Ti phase as compared to the growing Ni-Zr phase which limits the formation of amorphous alloys by means of solid-state reaction in the Ni-Ti system.

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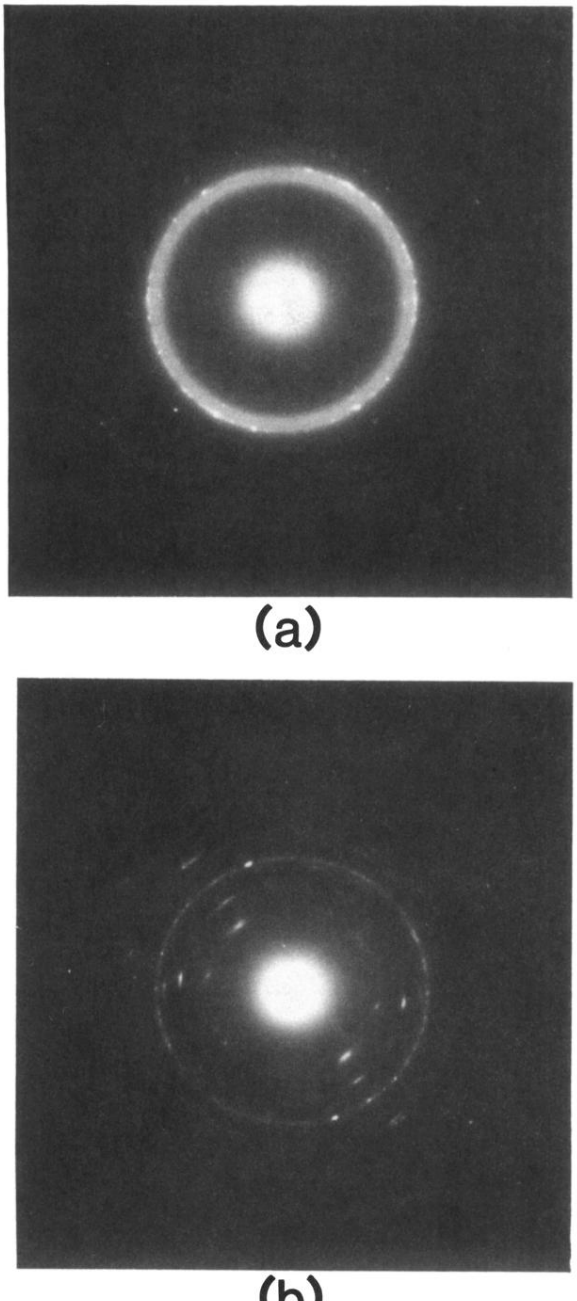

FIG. 5. Selected area diffraction patterns for a multilayered composite of Ni and Ti of average stoichiometry $Ni_{50}Ti_{50}$. Samples were examined in plane-view geometry with an electron microscope operated at 125 keV. (a) The sample after being heated at 10 K/min to a temperature of 670 K and rapidly cooled to room temperature in the differential scanning calorimeter. (b) A similar sample after being heated at 10 K/min to a temperature of 670 K and rapidly cooled to room temperature in the differential scanning calorimeter.