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Amorphization of Hf-Ni films by solid-state reaction

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We report on a detailed study of a new process to produce amorphous binary alloys by solid-state reaction of the elemental constituents from an initially thin-layer configuration. The Ni-Hf system was selected on the basis of the criteria that a fast diffuser (Ni) and a large binary heat of mixing drives the solid-state reaction at temperatures so low ($\sim 300\,^{\circ}\mathrm{C}$) that nucleation and growth of the crystalline phases are suppressed and the amorphous phase becomes the lowest accessible state of free energy. Backscattering spectrometry, x-ray diffraction, and transmission electron microscopy are used to monitor the atomic composition profile and the microstructure of the samples. The kinetics of the amorphous phase formation is consistent with the diffusion-limited growth of a laterally uniform amorphous layer. The substantial and approximately linear composition gradient of the amorphous layer reflects the low atomic mobility of the atoms in the amorphous phase and the broad existence range of the amorphous phase in the binary Ni-Hf system. The latter is consistent with predictions based on the calculated equilibrium free-energy diagram of the system.

I. INTRODUCTION

Amorphous materials are usually produced by rapid quenching of the melt or the mixed vapor phase. In both cases, high cooling rates are necessary to bypass crystallization and "freeze" the system in a metastable disordered phase. However, it has recently been demonstrated that amorphous materials can also be obtained under kinetic conditions of a rather different nature. A first example of this new approach was given by the formation of amorphous Zr_3Rh hydride by the diffusion at constant temperature of hydrogen into crystalline Zr_3Rh.[1] The success of this reaction was attributed to the fact that the high mobility of H with respect to the metallic constituents allows hydrogenation to take place below the temperature required for nucleation of crystalline Zr-Rh hydrides. It was argued that, although the amorphous hydride is intrinsically metastable, it is the lowest free-energy state achievable by the system under the given kinetic restrictions.

More recently, it was shown that a similar process involving only solid metallic constituents can also take place, in cases where one element exhibits an "anomalously fast diffusion" in the other.[2] However, the growth of the amorphous phase also requires a sufficiently large driving force to sustain the reaction. The simplest way to fulfill this condition is to look for binary systems exhibiting a large and negative heat of mixing in the solid state. Indeed, several systems selected on the basis of these two criteria (fast diffusion and large chemical driving force) were successfully amorphized by fast-diffusion reaction in the solid state, e.g., Au and La,[2] Y and Au,[3] Ni and Zr.[4] In the three cases, alternating thin layers of the pure-crystalline elements were evaporated to form multilayer films, which were heated under the appropriate time and temperature conditions. After the interdiffusion was completed, the resulting amorphous phase was characterized by x-ray diffraction and transmission electron microscopy (TEM).

The novelty of this procedure raises fundamental questions about the nature and the mechanism of the transformation taking place during the reaction process. For the first time, the growth of an amorphous phase can be followed over long time periods (minutes to hours) and compared with more familiar crystalline thin-film reactions. A powerful technique for the study of thin-film phenomena is backscattering spectrometry.[5] We have therefore used this technique to study the amorphization of thin multilayered polycrystalline films by diffusion reaction in the solid state. Our choice of a binary system was guided by the basic conditions stated above. In addition, care was taken to enhance the analytical power of the backscattering analysis by selecting a pair of elements with a large mass difference. For these reasons, we decided to perform our investigation on Ni-Hf multilayers: Ni is an anomalously fast diffuser in Hf,[6] the heat of mixing of both elements is large and negative (-60 kJ/g-at.),[7] and their large mass difference provides excellent conditions for backscattering spectrometry. Moreover, Ni-Hf glasses have been made by conventional quenching techniques and their properties have been extensively studied by x rays, resistivity, and other methods.[8]

II. EXPERIMENTAL

Ni-Hf multilayer films were prepared by electron-gun evaporation from metallic targets on thin pyrex and oxydized Si substrates. The vacuum in the evaporation chamber was brought into the 10^{-8}-Torr range prior to deposition by the combined operation of Ti-sublimation and ion pumps. The thickness of the individual layers varied between 100 and 400 Å, depending on the particular configuration under investigation. The films were thermally treated after being removed from the evaporation chamber. The vacuum in the annealing furnace was kept below 5×10^{-7} Torr. Most of the annealings took place between 300 and 340 °C.

The depth profile of the films was recorded before and after thermal treatment by backscattering spectrometry, using 2-MeV He^+ ions. Care was taken to keep the intensity of the analyzing beam sufficiently low so as not to cause substantial heating of the samples. Structural characterization of the reaction products was accomplished by x-ray diffraction, using a standard thin-film Read camera setup at a glancing angle with Cu $K\alpha$ radiation. Selected samples were also checked by transmission electron microscopy and electron diffraction.

III. RESULTS AND DISCUSSION

A. Morphology of reacted multilayers

Multilayer samples with overall composition $Ni_{20}Hf_{80}$, $Hi_{55}Hf_{45}$, and $Ni_{75}Hf_{25}$ were heated for 12 h at 340°C. All samples had a Ni layer on top. The reaction products are found to depend on sample composition in a way similar to that in the Au-La system.[2] For samples containing approximately equal amounts of Ni and Hf, a predominantly single-phase reaction product is obtained, whereas for Ni-rich or Hf-rich films the crystalline phase of the dominant component coexists with the single-phase product after reaction.

We checked the amorphicity of the reaction product by TEM and electron diffraction. The substrate was removed by acid jet thinning, and pictures were taken at the thinned edges of the metallic film. The electron micrograph of the reacted film shows a mostly uniform background with weakly contrasted spots of size ~100 Å (Fig. 1). This pattern is often seen in amorphous alloys; most recently, TEM studies on solid-state—reacted Ni-Zr have revealed weak remnants of the crystalline grain structure.[9] The electron-diffraction pattern exhibits the characteristic line broadening associated with the amorphous structure and a complete absence of Laue spots or sharp rings.

Backscattering analysis gives the mass distribution of the two components in the film as a function of depth. The amplitude of the backscattering signal of as-evaporated samples exhibits periodic modulations which are typical for multilayer structures (Fig. 2). The modulation amplitude is determined by the layer thickness and the depth resolution of the system. This depth resolution is influenced by various factors, including detector, electronics, mass and energy of the analyzing beam, atomic mass, and tilt angle of the target. Our estimated depth resolution at perpendicular beam incidence is about 150 Å. Since most individual layers are somewhat thicker than this, the spectra are sufficiently detailed to give a clear overall view of the film structure. Figure 2 also shows a spectrum of a reacted film with composition close to $Ni_{55}Hf_{45}$. The flatness of both Ni and Hf signals indicates a single homogeneously mixed phase, with small amounts of unreacted material near the surface. This picture is to be compared with Fig. 3, showing the backscattering spectrum of a film containing excess Ni before and after annealing. Although the individual layers are considerably intermixed after annealing (except for the top ones), the composition of the film is still inhomogeneous. The dips of the Hf signal correspond to Ni-rich regions, suggesting that most of the excess crystalline Ni remains concentrated in the original Ni layers. Details of the concentration fluctuations cannot be obtained from this spectrum due to insufficient depth resolution. Nevertheless, it can be clearly observed that the top layers of both Ni and Hf have not reacted. The same feature has occasionally been noticed on other annealed multilayers; we will discuss the origin of this effect below.

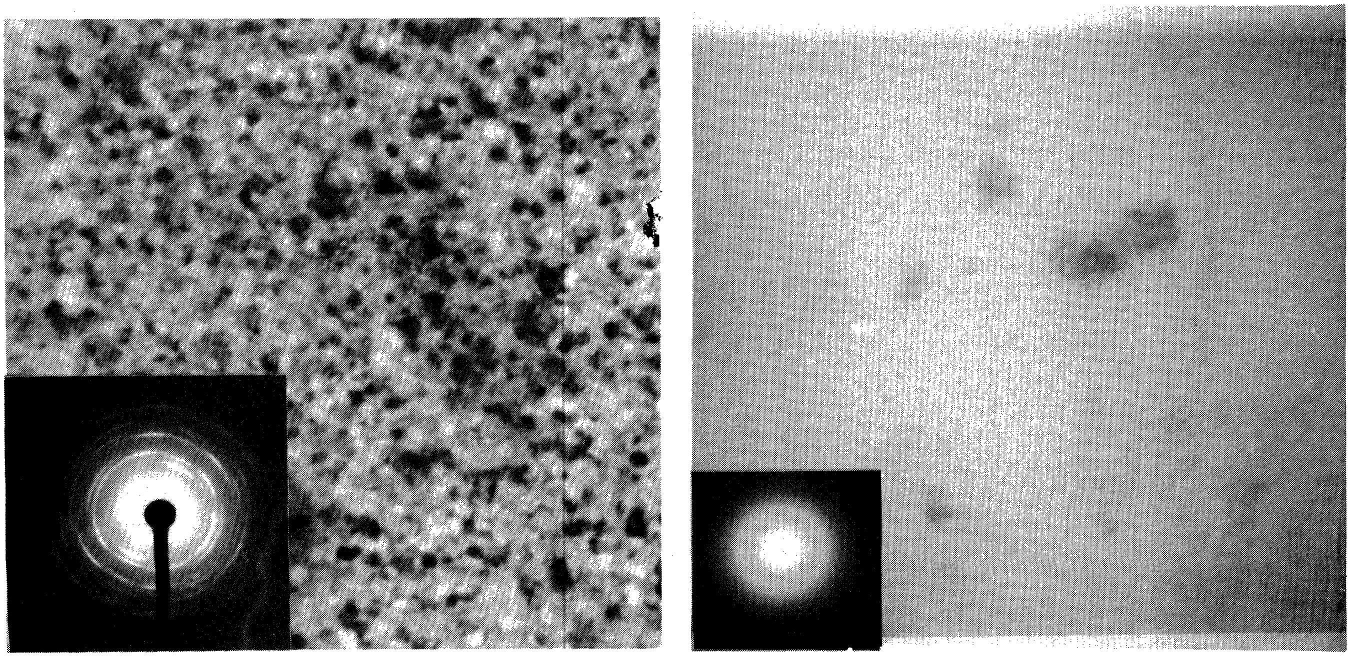

FIG. 1. Electron microphotograph and electron-diffraction pattern of a Ni-Hf multilayer film before (left) and after (right) solid-state reaction (1 cm = 2000 Å).

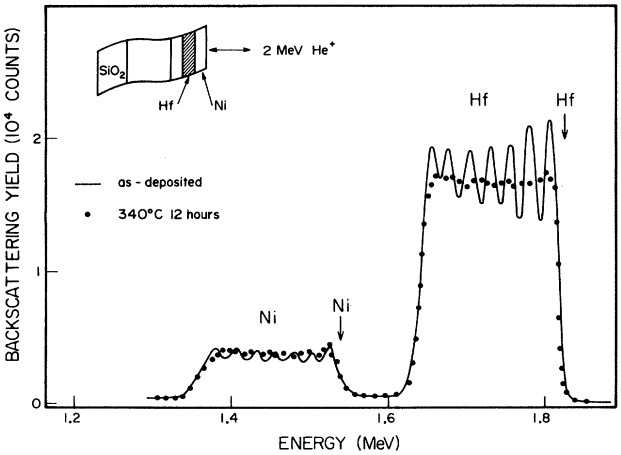

FIG. 2. Backscattering spectra of a $Ni_{55}Hf_{45}$ multilayer before and after solid-state reaction ($T=340\,°C$, $t=12$ h).

B. Discussion

The dependence of the solid-state reaction products on the composition of the original multilayers can be understood from considerations similar to those that govern the coexistence of crystalline phases in thermodynamic equilibrium. This is illustrated in Fig. 4, which displays the Gibbs free energy of the homogeneous amorphous phase (solid line) and of the unreacted multilayer system (dashed line) as a function of composition. The free energy of the amorphous alloy was obtained by extrapolating the corresponding values for the liquid phase (calculated in the random regular solution approximation) to temperatures in the undercooled regime. The free energy of the unreacted films was calculated as a weighted average of the pure-crystalline enthalpies of the constituents at the temperature of the reaction. Details regarding the calculation of both curves can be found in Refs. 2 and 3.

The difference in free energy between the amorphous phase and the unreacted multilayer provides the necessary thermodynamic driving force for the growth of the amorphous phase. Applying the common tangent rule from equilibrium thermodynamics to the diagram in Fig. 4 shows that a single-phase amorphous product can be expected over a substantial range of compositions. Outside the single-phase region, the common tangent rule predicts that the crystalline phase of the dominant component should coexist with the amorphous alloy. It should be noted that the proposed diagram does not include the free energies of the Ni-Hf crystalline intermetallic compounds, although they should be lower than the amorphous phase near the stoichiometric composition of the compounds. This omission is justified by the fact that kinetics appropriate to this problem allow the amorphous phase to grow below the temperatures at which nucleation and/or growth of crystalline compounds would become possible. Obviously, this kind of argument cannot exclude the nucleation of stable or metastable crystalline compounds which would compete with the amorphous-phase formation on the same time scale. Competition from crystalline phases with a relatively simple unit cell has indeed been observed during solid-state reaction of Y-Au.[3] However, our x-ray data on Ni-Hf reacted films have shown no trace of new crystalline compounds after the reaction.

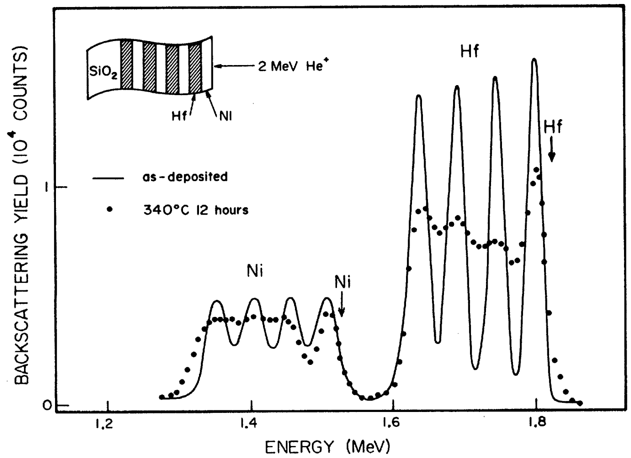

FIG. 3. Backscattering spectra of a $Ni_{75}Hf_{25}$ multilayer before and after solid-state reaction ($T=340\,°C$, $t=12$ h).

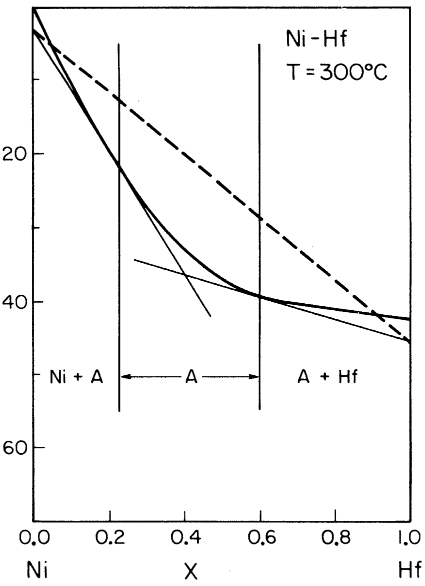

FIG. 4. Calculated Gibbs free-energy diagram of an unreacted (dashed line) and reacted (solid line) Ni-Hf film.

C. Detailed study of the interdiffusion process

Details of the amorphous-phase growth can be obtained by limiting the number of layers in the film and recording backscattering spectra at oblique incidence to increase the depth resolution. For this purpose, we prepared samples with two or three alternating layers of Ni and Hf. The samples were reacted under the same conditions as the thicker multilayer films. By performing backscattering analysis with a target tilt angle between 70° and 75°, the depth resolution of the system was improved to less than 50 Å. Within these experimental limits, we did not, in general, observe interdiffusion at temperatures below 350 °C in bilayers which had Ni on top. Trilayers with the configuration Ni-Hf-Ni showed interdiffusion at the deep interface only. The same was true for Hf-Ni-Hf trilayers, when the top Hf layers did not exceed 100 Å. On the other hand, bilayers with a top Hf layer exceeding 200 Å showed substantial interdiffusion.

These observations can all be explained by assuming that the surface of the film is contaminated with oxygen after removal from the evaporation chamber. It is presumed that the oxygen accumulates at the surface of the first available Hf layer and forms a diffusion barrier which inhibits the reaction. Once oxydized, this barrier also prohibits further oxygen diffusion, and therefore protects the deeper-lying interfaces. X-ray diffraction occasionally showed small traces of HfO_2 after reaction, but not in as-evaporated films.

D. Growth kinetics of the amorphous phase

We have studied the growth kinetics of the amorphous phase on a Hf-Ni-Hf trilayer, the top Hf layer playing the role of a protective cap. The choice of this configuration resulted from a compromise between the requirement of a clean interface and the necessity to limit the total thickness of the film in order to maximize the backscattering resolution. We performed heating sequences under isothermal as well as isochronal conditions. Spectra were taken after isothermal heating steps of 15, 30, 60, 120, 180, and 240 min at 340 °C. Some results of this sequence are displayed in Fig. 5. As expected, only the second Ni-Hf interface shows substantial interdiffusion. The progress of the reaction can most clearly be followed on the low-energy edge of the Ni signal. Three main characteristics of the reaction can be deduced from this spectrum and will be discussed below.

(i) A fairly sharp interface exists between the reacted and the unreacted portion of the film; the shape of this interface remains constant in time.

(ii) The growth of the amorphous phase takes place under an approximately constant gradient of composition in the amorphous film.

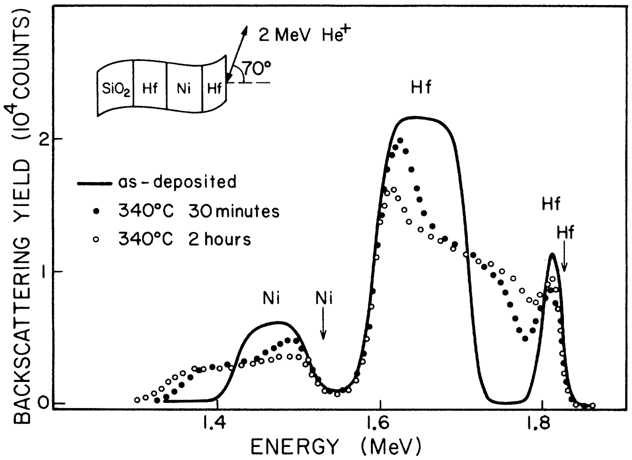

FIG. 5. Backscattering spectra of a 100-Å Hf—250-Å Ni—400-Å Hf film showing the progress of the solid-state reaction after 30 min and 2 h annealing at 340 °C.

(iii) The velocity of the interface does not exhibit a simple t or $t^{1/2}$ dependence.

The existence of a fairly sharp interface suggests answers to some fundamental questions concerning the formation and growth of the amorphous phase within the crystalline layer structure. As a simple limiting case, one could imagine a growth process that would start by heterogeneous nucleation at isolated "disorder centers" along the interface between the Ni and Hf layers. These isolated nuclei would then ultimately coalesce into a homogeneous amorphous region in a way analogous to the inverse process of crystallization of a metallic glass.[10] The growth speed of these islands would be controlled by the Ni diffusion along the amorphous/crystalline interface through the remaining Hf matrix. This of course would imply a rather uneven interface topology. Indeed, a sharp interface could only be conserved by assuming a highly correlated growth of the amorphous nuclei; such a complicated topological correlation seems rather improbable at this point. On the other hand, the observation of a sharp interface between unreacted and reacted material would result naturally from another limiting case according to which the amorphous layer would grow laterally uniformly over the whole amorphous-crystalline boundary, resulting in a high degree of lateral homogeneity at the interface. The Ni supply would be primarily provided by Ni diffusion through the growing amorphous Ni-Hf layer. We believe that this picture is favored by our backscattering results. The picture implies that only a small amount of atomic rearrangement is required at the interface to initiate the amorphous-crystalline transition.

The as-deposited thicknesses were 280 Å for the Ni and 400 Å for the Hf layer (not taking into account the Hf cap). This corresponds to an original average composition close to $Ni_{60}Hf_{40}$. After 4 h of diffusion, the reaction interface has approached the back of the Hf layer and the composition over the mixed region varies almost linearly from $Ni_{70}Hf_{30}$ to $Ni_{45}Hf_{55}$. The existence of a strong composition gradient is a peculiarity that is normally not observed when crystalline compounds are formed by solid-state reaction in similar multilayer structures. Moreover, the observed compositions fall well within the range in which the amorphous phase would exist in metastable equilibrium with the pure metals, according to the common tangent rule (Fig. 4). The fact that the experimentally observed range is narrower than the theoretically predicted one may be due to interface reaction barriers, to finite thickness effects in the samples and/or uncertainties in the free-energy calculations; further experiments should be able to clarify this point.

Another interesting property of the amorphous-phase growth is the fact that the composition gradient is roughly constant in space. In the analysis of thin-film interfacial reactions, it is usually assumed that the composition of the compound film varies linearly between fixed compositions at the interfaces,[11] as determined by interface reaction barriers and by the common tangent rule, i.e., by the equality of the chemical potentials on both sides of the reaction boundary. The usually narrow range of homogeneity of crystalline compounds makes it very difficult to observe any composition gradient experimentally. In our case, it is remarkable that the composition of a given slice of the amorphous layer does not change further once it has been formed. This probably reflects the large drop in the mobility of the reacting atoms after they have been trapped at their equilibrium position in the amorphous network. It is possible, however, that compositional redistributions may take place over time scales longer than those involved in our experiments.

The backscattering analysis also provides some information on the time evolution of the reaction, although the present data are insufficient to extract a reliable growth law. We have applied the formalism of thin-film reactions[11] to derive an approximate chemical interdiffusion coefficient from the initial shift of the reaction interface. Assuming a steady-state regime and diffusion-controlled growth, we obtain $D = 6\times10^{-19}$ m^2/s for the first 15 min of the reaction at 610 K. This value falls in the neighborhood of earlier diffusion data for Ag and Au diffusion in metallic glasses at comparable temperatures,[10] although it tends to be somewhat higher than the bulk of the reported data. By taking into account the smaller size of Ni versus Ag or Au, the similarity of these numbers suggests that the growth of the amorphous phase is, at least in its initial stage, controlled by the diffusion of Ni in the amorphous Ni-Hf layer. This same growth mode is supported by backscattering data, as discussed in connection with Fig. 5.

As the reaction evolves, the deviation from a $t^{1/2}$ growth law becomes more pronounced (see Fig. 6). Since the Ni supply is finite, one should expect a changeover in the growth law as one metal is consumed, leading ultimately to an exponentially decaying flux as the composition profiles relax towards uniformity. The latter regime was not investigated in the present study.

Finally, we also performed isochronal annealing treatments on the same trilayer configuration (Fig. 7). Samples were heated for 30 min at temperatures varying between 260 and 380 °C. The onset of the reaction was observed between 290 and 300 °C. In the absence of a well-established growth law, we did not attempt to determine the activation energy of the reaction. It can be observed that the composition gradient in the reacted layer depends on the reaction temperature. It would clearly be of interest to extend these measurements towards higher temperatures, particularly, near the recrystallization temperature of the amorphous phase.

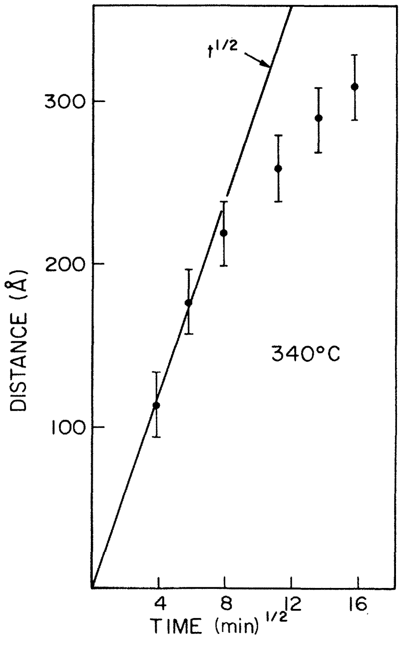

FIG. 6. Position of the Ni interface (same sample as Fig. 5) as a function of reaction time.

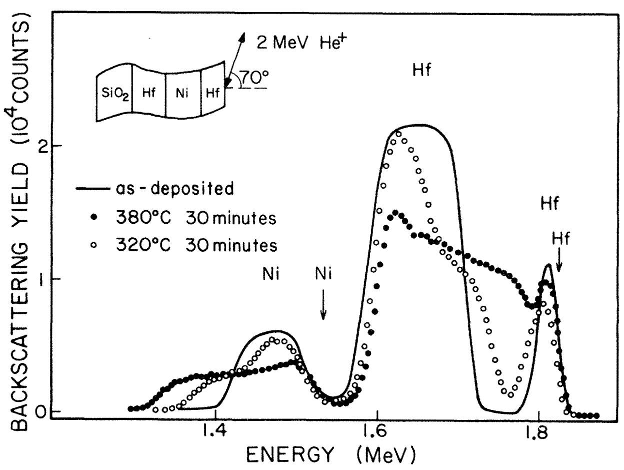

FIG. 7. Backscattering spectra of a Hf-Ni-Hf film (same sample as Fig. 6) reacted at various temperatures.

IV. CONCLUSION

The present study substantiates the validity of the process of diffusion in the solid phase as a new mode by which amorphous binary alloys can form. The fast diffusion of one species in the crystalline phase of the other, at temperatures sufficiently low to suppress nucleation and growth of crystalline compounds, appears to be a useful criteria for identifying favorable systems. The amorphous state then becomes the lowest free-energy state that is kinetically accessible. A large negative heat of mixing provides a strong driving force that favors the interdiffusion process and the formation of an amorphous phase. Free-energy arguments that treat the amorphous state as an equilibrium phase can be used to predict the range of existence of the amorphous phase and the existence of two-phase regions near the terminal compositions by applying the common tangent rule.

The solid-state reaction in multilayer Ni-Hf films has been analyzed within the framework of thin-film reaction phenomena. From this point of view, our observations represent a first step towards the description of a new class of thin-film reactions. Some fundamental characteristics of the amorphous-phase formation were established, e.g., the uniform growth of the amorphous layer at the reaction boundary and the existence of an approximately constant composition gradient over the reacted layer. Finally, these results also provide some insight into the nature of the crystalline-to-amorphous transition in the solid state. The sharpness of the amorphous/crystalline interface proves that the transition towards amorphicity can be achieved in a crystalline matrix by a local atomic rearrangement process at the reaction boundary. This raises several questions regarding the mechanism by which the amorphous-phase growth is initiated; in particular, whether or not the initial interface serves as a heterogeneous nucleation site. The fact that the composition range of the amorphous compound obeys the general rules of phase equilibria in solids, clearly generalizes earlier considerations on the compositional limitations of the amorphous phase. More specifically, it implies that criteria involving near-eutectic compositions (as in liquid quenching[12]) are imposed by the particular choice of the kinetics, but are of no general thermodynamic significance for the amorphous-phase formation.

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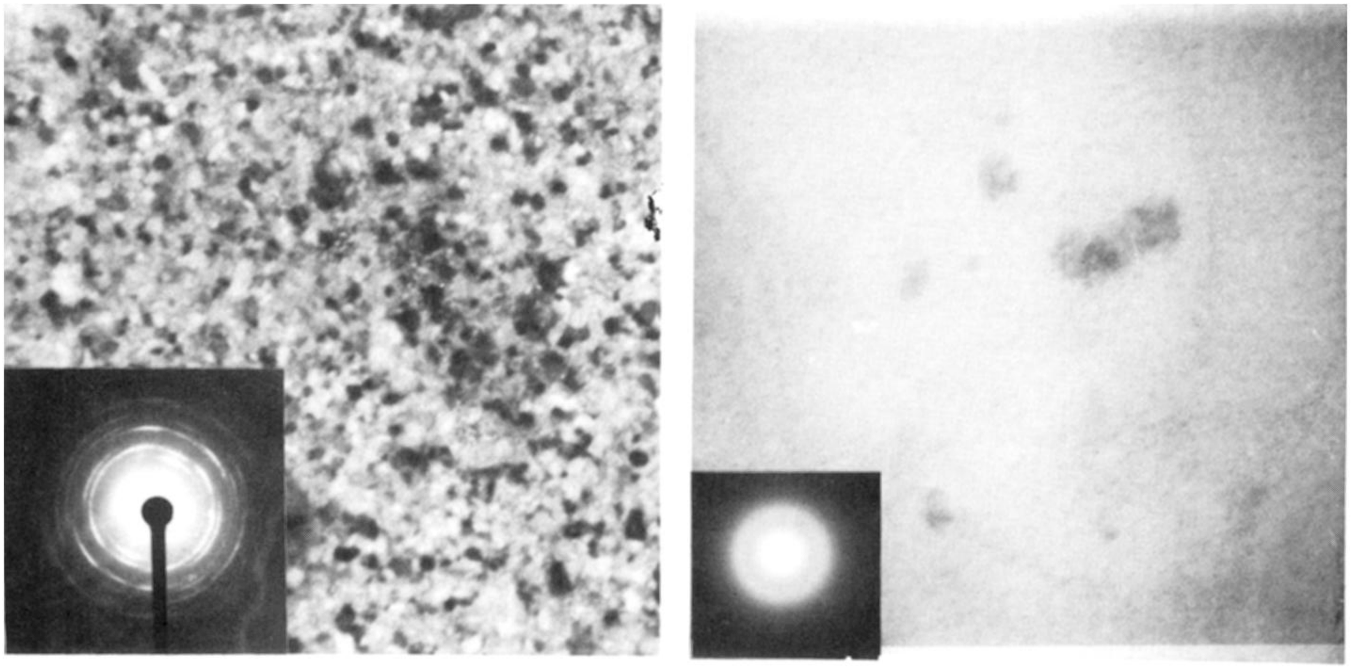

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