

Maximum thickness of amorphous NiZr interlayers formed by a solid-state reaction technique

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Formation of the equilibrium intermetallic compound NiZr in sputter deposited Ni/Zr diffusion couples is suppressed by the formation of a metastable amorphous NiZr alloy until a critical thickness of the amorphous NiZr interlayer is reached. The temperature dependence of this critical thickness is studied experimentally. A phenomenological model based on the premise of interfacial heterogeneous nucleation is proposed to understand the evolution of Ni/Zr diffusion couples.

Compound formation in binary, planar, thin-film diffusion couples by solid-state interdiffusion often proceeds by the sequential formation and growth of equilibrium phases. It is often found that the first phase grows to a critical thickness before the second phase forms and similarly for successive phases. Most studies in this area have concentrated on metal-silicon diffusion couples where the phases formed belong to the equilibrium phase diagram.¹ Recent studies of metal-metal diffusion couples have shown that a metastable amorphous phase may form initially and grow to substantial thickness prior to the onset of formation of crystalline intermetallics.² In the Ni-Zr system, an amorphous NiZr alloy (*a*-NiZr) is observed to form and grow to a critical thickness $X_c \sim 100$ nm prior to the appearance of the equiatomic crystalline intermetallic compound NiZr (*c*-NiZr).³⁻⁵ We have carried out isothermal reactions over a range of temperatures and times to determine whether this critical thickness is temperature dependent and to understand the microscopic origin of the critical thickness. The technique of cross-sectional transmission electron microscopy (XTEM) is used to follow the evolution of the diffusion couple. In a closely related study,⁶ we have also examined how the use of single-crystal Ni and Zr starting layers in place of polycrystalline films influences the evolution of the diffusion couple. Taken together, these studies provide a critical test of current models⁷ for evolution of diffusion couples.

Growth of *a*-NiZr occurs at rather low temperatures (~ 200 – 300 °C). The collective atomic rearrangements required for crystallization within the already formed amorphous interlayer do not occur until much higher temperatures are reached. The transition from growth of *a*-NiZr to *c*-NiZr occurs *heterogeneously* at the moving *a*-NiZr/Zr interface; any factors which influence this moving interface would therefore influence this transition. Among these factors, both Kirkendall void formation in the elemental Ni layer at the Ni/*a*-NiZr interface,⁵ and structural relaxation in the growing *a*-NiZr interlayer⁸ could reduce the *a*-NiZr/Zr interface velocity and therefore may both be relevant. However, by reacting single crystals of Ni with Zr, where the formation of Kirkendall voids is suppressed, we have also observed compound formation when amorphous interlayers reached ~ 100 nm.⁶ Thus it appears that voids in the Ni layers are not essential for the termination of amorphous interlayer growth. In what follows, we present our experi-

mental observation of the temperature dependence of the critical thickness of *a*-NiZr and propose a simple phenomenological model based on the premise of *interfacial heterogeneous nucleation* and show how the suppression of NiZr compound formation by the growth of *a*-NiZr can be understood in this framework.

Ni/Zr multilayered thin films were prepared by a dc magnetron sputtering technique described elsewhere.³ Alternating layers of Ni and Zr were deposited onto an oxidized silicon substrate. Heat treatments were carried out in a vacuum furnace with pressure less than 5×10^{-7} Torr. Heat-treated samples were subsequently prepared for XTEM study following the procedures outlined by Sheng and Chang.⁹ These cross-sectional specimens were examined with a Philips EM 430 transmission electron microscope operated at 300 kV and equipped with an energy-dispersive x-ray analyzer.

A XTEM bright-field micrograph of a typical Ni/Zr thin film is shown in Fig. 1. The specimen was briefly heat treated ~ 200 °C. The as-deposited microstructure of both the pure Ni and pure Zr layers, as well as a very thin *a*-NiZr interlayer originating at each Ni/Zr interface, is clearly evident. The growth of the *a*-NiZr interlayer is captured at a relatively early stage. Amorphous interlayers are less than 10 nm in thickness and are laterally very uniform.

Figure 2 shows a XTEM bright-field micrograph of a Ni/Zr multilayer annealed at 320 °C for 8 h. A section of the original sample is shown in the micrograph. In addition to the *a*-NiZr interlayers, which are now about 100 nm in thickness, NiZr compound layers about 100 nm in thickness can be seen to have formed between the *a*-NiZr and the remaining Zr layers. Microdiffraction from the compound layer is consistent with the compound being NiZr. Energy-dispersive x-ray analysis indicates that the average composition of the amorphous layers is about Ni₆₀Zr₄₀ whereas that of the compound layers is close to Ni₅₀Zr₅₀. The *a*-NiZr/*c*-NiZr interface is relatively immobile at this low temperature, and the compound does not grow back into the amorphous phase appreciably. Heat treatments have been carried out at several different temperatures. The duration of heat treatment at each temperature is sufficient to have produced *c*-NiZr after *a*-NiZr interlayers have reached their maximum thickness. The results are tabulated in Table I.

The growth of the *a*-NiZr interlayers has been shown to

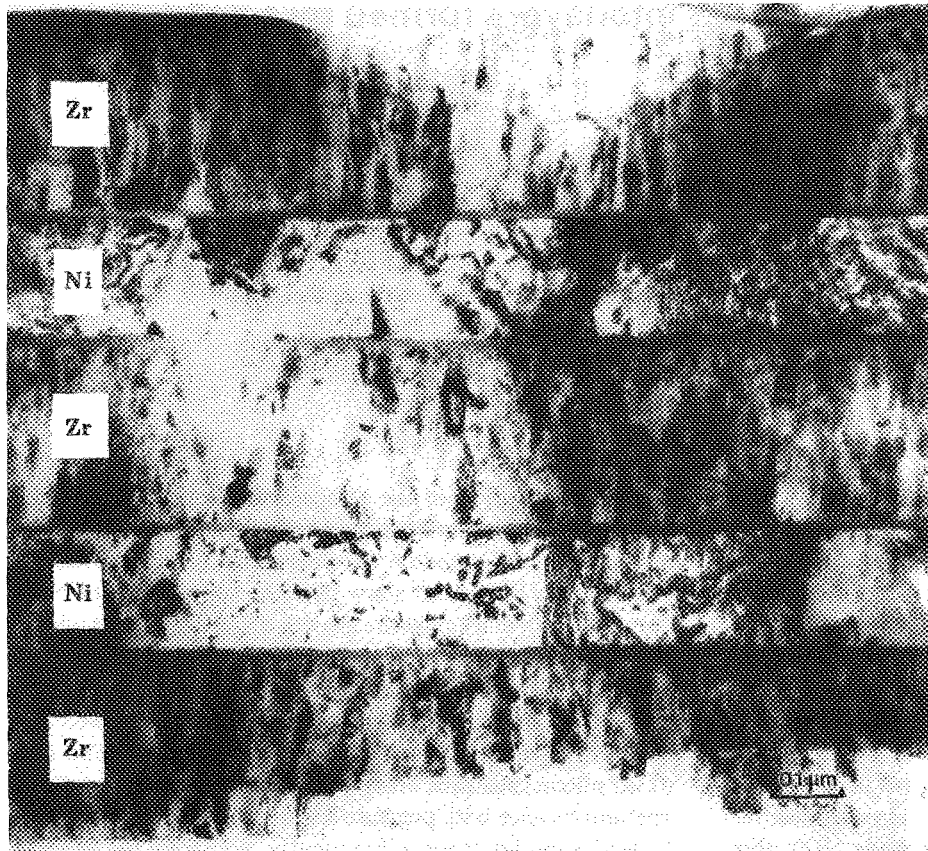


FIG. 1. Cross-sectional transmission electron microscopy (XTEM) bright-field micrograph of a Ni/Zr multilayered thin film annealed briefly around 200 °C.

be diffusion controlled and follows a " $t^{1/2}$ " time dependence.^{3,4} The fact that the α -NiZr interlayers grow only to a certain thickness before c -NiZr appears therefore signifies that at a given temperature the transition from the growth of an amorphous phase to that of a crystal happens at a mini-

mum α -NiZr/Zr interface velocity. Since a certain time scale is associated with the nucleation of the NiZr compound, the problem of when the compound phase will appear can be elucidated by examining two competing time scales in this problem.

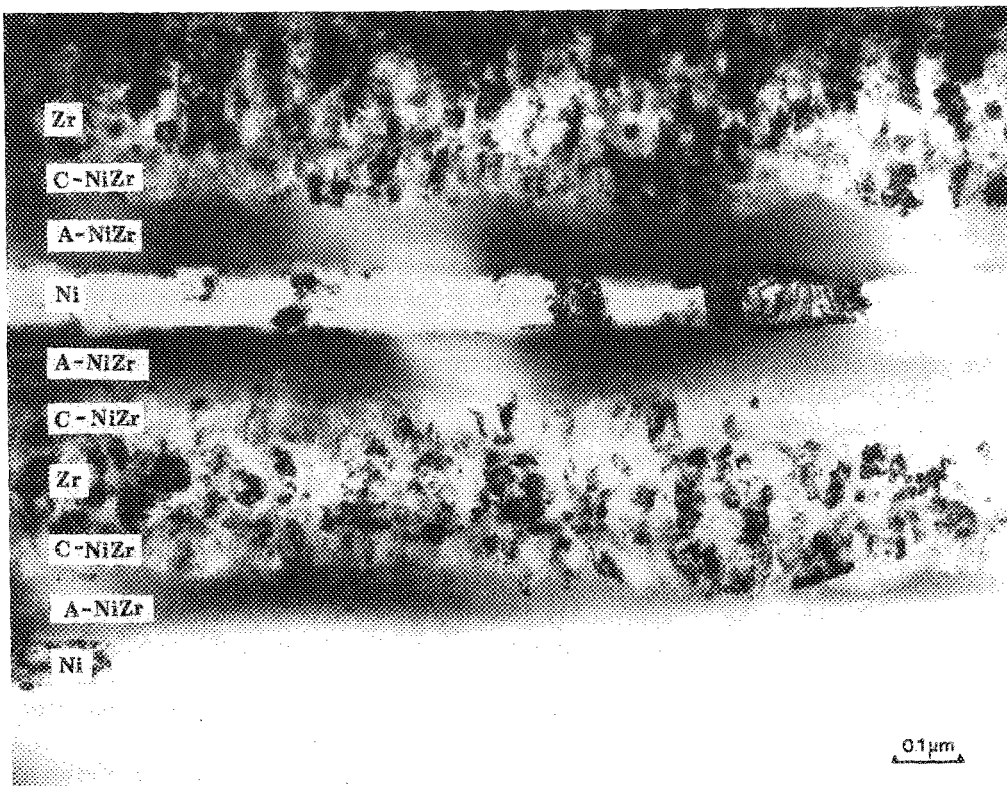


FIG. 2. XTEM bright-field micrograph of a Ni/Zr multilayered thin film annealed at 320 °C for 8 h. Both amorphous and compound interlayers are clearly evident. Amorphous interlayers are close to 100 nm in thickness.

TABLE I. Observed maximum thicknesses of amorphous NiZr interlayers prior to crystalline NiZr formation. Conditions of heat treatments: temperature T , duration t . x_{am} is the maximum amorphous NiZr interlayer thickness as observed by XTEM.

T (°C)	t (min)	x_{am} (Å)
300	720	980
320	480	950
340	90	900
360	10	870

Formation of any NiZr compound phase at a -NiZr/Zr interface requires formation of a heterogeneous nucleus. Assuming this to be the rate-limiting step in compound formation, we can analyze this transition. Since the growth of the a -NiZr interlayer is one dimensional, the relevant dimension of this compound critical nucleus is its thickness in the growth direction, denoted by L . Denote further the velocity of the a -NiZr/Zr interface during growth of a -NiZr interlayer as v_{int} . These parameters define a natural time scale τ_{int} required for the necessary atomic rearrangements taking place at the a -NiZr/Zr interface to form the NiZr compound nucleus

$$\tau_{int} = L/v_{int}. \quad (1)$$

In time τ_{int} , the amorphous interlayer would advance a distance of L , leaving behind the interface an immobile glassy atomic configuration. The competing time scale τ_{nuc} for formation of the NiZr compound at the a -NiZr/Zr interface can be taken as the inverse of the heterogeneous nucleation rate I . According to the classical steady-state nucleation theory, this nucleation rate I is given by

$$I = K\nu \exp\left(-\frac{\Delta G^* + Q}{k_B T}\right), \quad (2)$$

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 the heterogeneous nucleation barrier.¹⁰ The condition for the continued growth of the amorphous interlayer can be stated simply as an inequality between these two time scales

$$\tau_{int} \leq \tau_{nuc}, \quad (3)$$

where the equality denotes the critical condition when the formation of the compound becomes possible. Equation (3) dictates a lower critical a -NiZr/Zr interface velocity L/τ_{nuc} below which the growth of the amorphous phase cannot be sustained against nucleation of the intermetallic compound.

Equation (3) originates from general considerations of the two competing kinetics of amorphous phase growth and compound nucleation. Since the growth of the amorphous interlayer is diffusion controlled, the a -NiZr/Zr interface velocity can be related to the thickness of the a -NiZr interlayer x_{am} by

$$v_{int} = K'D_{am}/x_{am} \quad (4)$$

where K' is a dimensionless constant and $D_{am} = D_0 \exp(-Q/k_B T)$ is the interdiffusivity through the a -NiZr interlayer.⁷ An explicit expression limiting the thickness of the growing a -NiZr interlayer can be reached in this case

$$x_{am} \leq \left(\frac{K'D_0}{LK\nu}\right) \exp\left(\frac{(\Delta G^* + Q) - Q'}{k_B T}\right), \quad (5)$$

where the equality yields our prediction for the a -NiZr critical thickness X_c . It is to be emphasized that Eq. (5) is obtained under the assumption that the diffusion constant is time independent up to the transition between amorphous phase growth and compound nucleation, and this can be invalidated by effects such as structural relaxation in the amorphous phase during growth.

We have shown how the sequential appearance of phases in Ni/Zr diffusion couples can be understood by assuming that the nucleation of the compound NiZr is the limiting factor for amorphous phase growth. An alternative notion of *interfacial reaction barriers* has been introduced previously by Gosele and Tu. It has been argued that even in the absence of nucleation barriers, certain phases would be kinetically unstable due to the presence of interfacial reaction barriers.⁷ The relevance of both models needs to be clarified by further experimentation.

In summary, we have examined the formation of an amorphous NiZr alloy as well as the subsequent formation of the compound NiZr by cross-sectional transmission electron microscopy. A simple phenomenological model based on the premise of heterogeneous nucleation of the NiZr compound at the a -NiZr/Zr interface is suggested, this model is used to understand the critical thickness for growth of the amorphous phase.

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