Crystallization of amorphous Ni$_{60}$Nb$_{40}$

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The crystallization of Ni$_{60}$Nb$_{40}$ metallic glass during continuous heating and isothermal annealing at temperatures from 845 to 904 K, was studied by differential scanning calorimetry (DSC), electrical resistance measurements, X-ray diffraction and transmission electron microscopy. Crystallization occurred in four clearly defined stages. In the initial stage a metastable phase, with structure similar to the M-phase in the Ni–Nb–Al ternary system, forms in the amorphous matrix. In the two subsequent stages the remaining glass crystallizes to the Ni$_3$Nb- and μ-phases found in the equilibrium Ni–Nb phase diagram. The M-phase transforms into the equilibrium Ni$_3$Nb- and μ-phases only at high temperature. The crystallization of the M-phase could be described by Johnson–Mehl–Avrami kinetics with the time exponent $n = 1.3$ and activation energy $E_1 = 628$ kJ mol$^{-1}$. M-phase crystal growth was apparently diffusion controlled and the diffusion coefficient was estimated to be $4.2 \times 10^{-20}$ m$^2$ sec$^{-1}$. Activation energies for the second and third stages of crystallization were found to be $E_2 = 446$ kJ mol$^{-1}$ and $E_3 = 430$ kJ mol$^{-1}$.

1. Introduction
The crystallization of metallic glasses is a topic of considerable interest. Technologically, the subject is of importance since the properties of the glass may be changed significantly by the onset of crystallization, and the utilization of the glass is thus limited by the conditions of time and temperature at which crystallization occurs. Scientifically, the crystallization of metallic glasses provides an opportunity to study the nucleation and growth of crystalline phases under conditions far removed from equilibrium.

To date, although there have been numerous studies of crystallization behaviour of metal–metalloid glasses, few studies of metal–metal glasses have been reported. The purpose of the present study was to examine in detail the crystallization of the amorphous Ni$_{60}$Nb$_{40}$ alloy. This behaviour has been treated briefly in previous papers [1, 2] and the intent of the present work is to examine in greater detail the structural changes occurring during crystallization using X-ray diffraction and transmission electron microscopy (TEM). Transformation kinetics were determined over a wide temperature range using electrical resistance measurements and differential scanning calorimetry (DSC).

2. Experimental details
Amorphous ribbons were prepared by a melt spinning technique. 10 g buttons of the alloy Ni$_{60}$Nb$_{40}$ were prepared by melting appropriate quantities of nickel and niobium (99.95% and 99.9% purity, respectively) in a nonconsumable vacuum arc furnace. After repeated melting to ensure chemical homogeneity the buttons were placed in an alumina crucible through the base of which a 1 mm pouring hole had been drilled. The charge was heated by induction in a helium atmosphere to 1675 K and the molten metal was ejected using a pressure of 55 kPa onto the inner rim surface of a copper wheel rotating at 40 m sec$^{-1}$. The ribbons produced in this manner averaged 30 to 40 μm in thickness and 2 mm in width. X-ray and TEM examinations failed to reveal any evidence of crystallinity in the as-quenched ribbons.

Differential scanning calorimetry experiments were carried out on a Perkin-Elmer DSC-2 calorimeter. The temperature scale was calibrated to

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within ± 1 K using K₂SO₄ and K₂CrO₄ standards and baseline sensitivity of 5 mcal sec⁻¹. The samples (typically 4 to 6 mg) were contained in graphite pans; alumina was used as a reference material. Heating rates from 1 to 80 K min⁻¹ were used.

Annealing kinetics were determined from isothermal electrical resistance measurements using a four-point probe system in which platinum leads were spot welded to the 2 cm long samples. The assembly was enclosed in a Vycor tube which was then evacuated prior to heating in a resistance tube furnace. Once placed in the furnace, the sample came to temperature in approximately 10 min; throughout the remainder of the experiment the temperature varied by less than ± 1.5 K. A constant current of approximately 5 mA was maintained throughout the experiment. A strip chart recorder was used to monitor electrical resistance as a function of time during each of the 13 tests performed at temperatures between 845 and 905 K.

In order to determine the structural changes indicated by the observed variations in resistance, samples were encapsulated in evacuated Vycor tubes and isothermally annealed for various times at 871 K. Subsequent to annealing the samples were examined by X-ray diffraction and TEM. The thin foils for TEM observations were prepared by a window technique in which the samples were electropolished at 54 V in a bath of 10% H₂SO₄ in methanol at 223 K. The thinned samples were examined in a Philips EM 300 microscope. A number of the isothermally annealed samples were scanned in the DSC to determine if the structural relaxation expected during annealing would alter the crystallization process in any way.

3. Results

3.1. DSC measurements

A typical DSC scan of the as-quenched Ni₆₀Nb₄₀ is shown in Fig. 1. At a heating rate β = 20 K min⁻¹ three distinct exothermic peaks are observed at 940, 980 and 994 K. The initial crystallization exotherm obscures the glass transition, but at higher heating rates a decrease in heat capacity, typical of the glass transition, was evident prior to the onset of crystallization. The calorimeter was limited to a maximum temperature of 1000 K and consequently the third peak is incomplete. It is not clear from the DSC results if further transformations would occur at higher temperature.

Using the method of Kissinger [3], the apparent activation energy for each step of the crystallization process was obtained from the slope of a plot of log \( T_p^2/\beta \) against \( 1/T \) (Fig. 2), where \( T_p \) is the peak temperature in the DSC thermogram obtained at heating rate \( \beta \). The deviation from linearity at high heating rates is probably due to