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Amorphous Structures in the Immiscible Ag-Ni System

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Vapor quenching in the phase-separating Ag-Ni system creates alloys that appear homogeneously amorphous under conventional probes. However, an atomic-level structural analysis based on extended x-ray absorption fine structures in combination with reverse Monte Carlo and molecular dynamics simulations demonstrates that these new phases are characterized by nonuniform, spinodal-like structures on an extremely fine scale. This heterogeneous nature of the structure is directly responsible for the unexpectedly low heat (and temperature) of crystallization observed in calorimetric measurements.

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The majority of amorphous alloys produced until now are in easy glass-forming systems exhibiting a negative heat of mixing $(-\Delta H)$ [1,2]. In these systems, the large thermodynamic driving force drives the constituent elements to spontaneously intermix to maximize the number of unlike bonds. The amorphous phases formed are thus alloyed on the atomic level and often characterized by short-range ordering. In fact, the local atomic structure within the nearest neighbors often resembles those in highly stable equilibrium compounds. As a result, the metastable amorphous alloy is a supercooled liquid with an excess specific heat and stabilized to an energy state close to that of the compounds, resulting in a heat of crystallization typically of only a few kJ/mol [1,2].

Over the years, there have also been reports of amorphous phase formation in $+\Delta H$ and even immiscible systems [3–9]. Any amorphous alloy that forms in such systems, in contrast to the $-\Delta H$ case, has to survive the large $+\Delta H$ that drives phase separation. The nature of these $+\Delta H$ alloys is thus interesting but remains poorly understood. One view is that such phases are unstable and simply kinetically frozen liquids far from equilibrium. The alloy is often assumed to be homogeneous under polymorphic constraints in a hard freeze, with an energy possibly as high as that of a directly extrapolated liquid. Also possible is that some degree of energy minimization is realized through the development of local structures that resemble equilibrium solids, even though long-range chemical partitioning is suppressed during quenching. In this case, however, one has no clue *a priori* as to exactly what atomic configurations to expect and the magnitude of the associated energy reduction, as there are no known structural arrangements, such as those in the $-\Delta H$ compounds, that would provide low-energy states for the alloy. Particularly interesting is the recent proposition that the undercooled liquid (amorphous) Cu-Nb can even exhibit a $-\Delta H$ at low temperatures even though the liquid of the same composition shows a $+\Delta H$ at high temperatures [10]. It is thus of fundamental interest to explore when and what kind of amorphous alloys can be formed between elements immiscible in equilibrium, and how different such $+\Delta H$ phases are from the well studied $-\Delta H$ metallic glasses. Such studies are also of significance to the research on bulk metallic glass-forming systems [2], where the overall composition often lies in a miscibility gap, and relevant to the understanding of $+\Delta H$ systems that are commonly used to prepare heterogeneous structures with functional properties such as the giant magnetoresistance.

In this Letter, we use vapor quenched Ag-Ni, a system with $+\Delta H$ and immiscible even in the liquid state, as a model of the alloys created in a highly phase-separating system. Our emphasis is to unravel the nature of such new alloys by revealing their unusual atomic-level structures and directly correlating the structural features with their energy states. Several complementary techniques, particularly the extended x-ray absorption fine structure (EXAFS) together with computer atomistic simulations as a local environment probe, have been used for characterization. Note that most previous studies on $+\Delta H$ alloys employed conventional tools used for $-\Delta H$ systems such as x-ray diffraction (XRD) and conventional transmission electron microscopy (TEM) that can hardly prove alloying or reveal structures on the atomic level. In addition, few experiments were accompanied by compositional analysis to rule out the possibility of impurity contamination that might have contributed to the stabilization of any new phase reported to form [7,8]. In the following, we demonstrate that the Ag-Ni alloy, while apparently amorphous similar to the $-\Delta H$ counterparts under conventional probes, is characterized by an ultrafine heterogeneous structure due to decomposition. The atomic scale structural feature are correlated with, and used to explain, the anomalously low heat of crystallization and crystallization temperature observed.

Foils of various compositions with thickness up to 10 μm were prepared using dc sputtering of a composite target employing different deposition parameters. Liquid nitrogen cooled Si wafers were used as substrates in a system with a base vacuum of 1×10^{-8} Torr. Solid solutions formed at both the Ag-rich and Ni-rich compositions [11,12], and amorphous alloys appeared in the central

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composition range at a deposition current of 100 mA and an Ar pressure of 5 mTorr ($Ag_{40}Ni_{60}$ is discussed below as an example). The typical "x-ray amorphous" feature is shown in the XRD pattern in Fig. 1. The film is also apparently amorphous upon observations of the high-resolution TEM image acquired in a Philips CM300 microscope operating at 300 kV, also displayed in Fig. 1 (the possible existence of short to medium range features is discussed below). Few diffraction spots were observable in the Fourier transforms of the image, and lattice fringes became visible only after prolonged irradiation under the focused electron beam, signaling the onset of long-range ordering (crystallization) of an originally amorphous film. The isothermal differential scanning calorimetry (DSC) curves (Fig. 2) exhibit a bell shape, characteristic of a nucleation and growth process during crystallization, rather than simple coarsening from preexisting nanocrystals [13]. The constant-heating-rate DSC trace in Fig. 2 displays a sharp peak indicative of crystallization, with a quite low crystallization temperature of 132 °C, followed by a broad peak typical of grain growth. The heat of crystallization integrated for both peaks is only 10.9 kJ/mol, a very low value compared with the enthalpy of a frozen liquid that would release heat in excess of 30 kJ/mol upon crystallization to fcc Ag and Ni [14]. The sample composition was confirmed by Auger electron spectroscopy, and impurity (oxygen, carbon, and argon) contents are all below the detection limit (about 1 at. %).

As determined in a SQUID (superconducting quantum interference device) magnetometer, the $Ag_{40}Ni_{60}$ alloy is ferromagnetic with a Curie temperature as low as 70 K, completely different from that of 627 K for Ni or about 400 K for a 1.1 nm thick Ni layer [15]. Also, no giant magnetoresistance was observable at 5 K, further ruling out the existence of granular Ni. In addition, by comparing zero-field-cooled and field-cooled magnetization as a function of temperature, we ruled out the possible existence of isolated Ni nanoclusters that would otherwise exhibit superparamagnetism. These measurements suggest that Ni atoms are indeed alloyed with Ag, and any aggregates would have effective diameters no larger than a fraction of a nanometer [15].

EXAFS experiments were carried out at room temperature at the Louisiana State University Center for Advanced Microstructures and Devices (LSU-CAMD) electron storage ring operating with a beam energy of 1.3 GeV and an injection current of ~180 mA. Figure 3 displays the Fourier transforms of the Ni K edge and the Ag L_{III} edge EXAFS (spectra in inset). The first neighbor peak amplitudes were reduced significantly compared with the crystalline element (by a factor of 3–4), and all the higher-order coordination shells were disrupted, a feature consistent with an amorphous material. However, signs of splitting peaks (shoulders) are observed around the usually nearest neighbor positions [16], suggesting possible short-range structures, e.g., different bond lengths and local environments. To solve the atomic scale structure, the methodology of reverse Monte Carlo (RMC) simulation [17,18] was used because in the case of such a disordered system, particularly when the Gaussian shape of the peaks in the radial distribution function (RDF) is poorly obeyed, it is difficult to obtain reliable structural parameters using

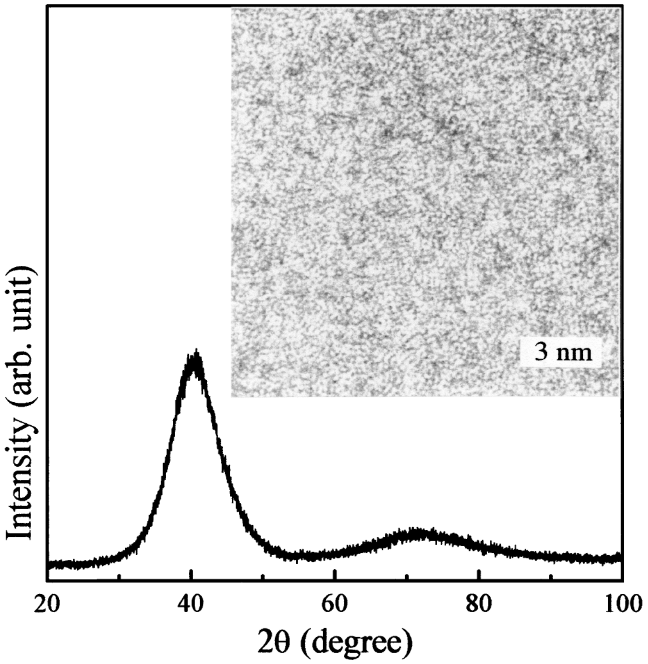

FIG. 1. X-ray diffraction pattern and high-resolution electron micrograph (inset) of the $Ag_{40}Ni_{60}$ alloy.

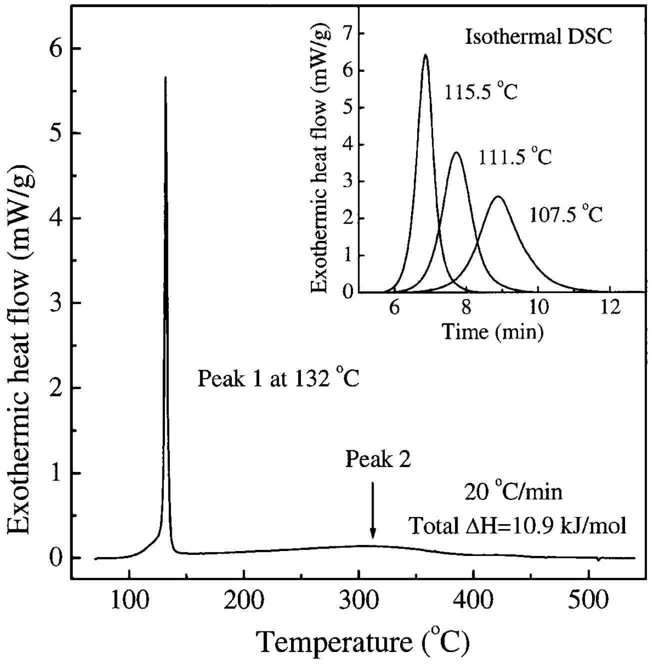

FIG. 2. Isothermal (inset) and constant-heating-rate DSC traces showing crystallization of the $Ag_{40}Ni_{60}$ foils.

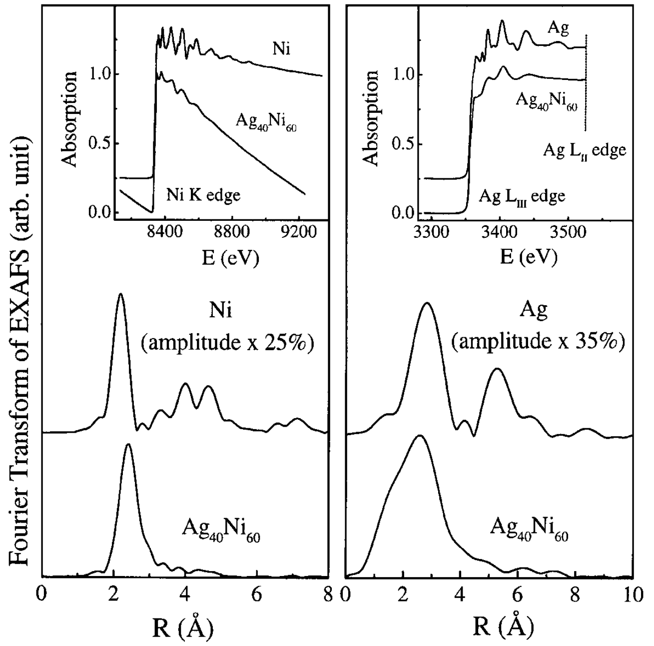

FIG. 3. Fourier transforms of the EXAFS of the $Ag_{40}Ni_{60}$ alloy at the Ni K edge and Ag L_{III} edge, compared with those of the crystal elements. Insets show the EXAFS spectra taken in transmission mode.

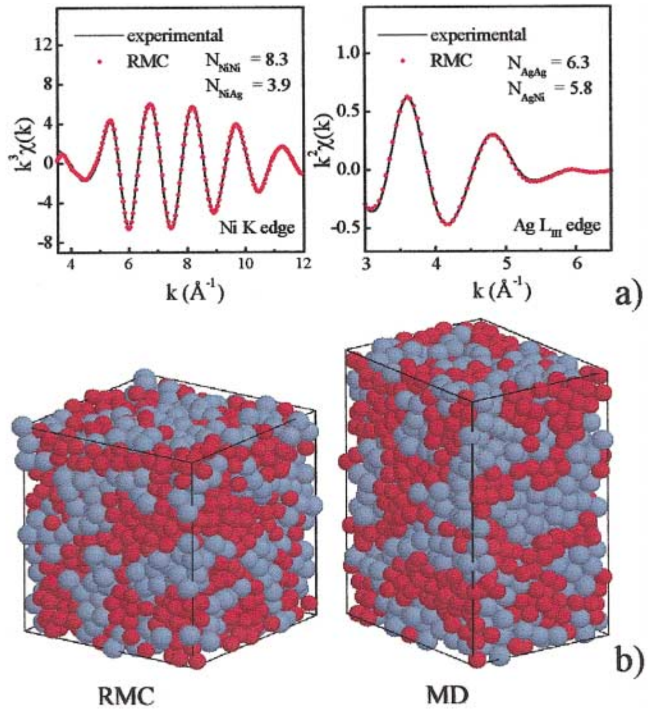

FIG. 4 (color). (a) Comparison in k space of the experimental EXAFS of $Ag_{40}Ni_{60}$ with that of RMC simulated structure. (b) Atomic configuration (Ni in red) in the RMC model (left) compared with that of amorphous $Ag_{40}Ni_{60}$ obtained in MD (right, see text).

conventional EXAFS fitting routines such as the cumulant expansion method. In RMC, an atomic configuration in a box of 2048 atoms for $Ag_{40}Ni_{60}$ with periodic boundary conditions was constructed and its EXAFS function calculated in single scattering approximation. In subsequent MC steps, new and improved configurations were adopted by optimizing a "quality of hit" function that represents the "distance" between the simulated EXAFS and the experimental one, eventually reaching a good match as shown in the k-space plots in Fig. 4(a). The resulting structure is presented in Fig. 4(b). It can be directly observed that the alloy is *not* homogeneous and has heterogeneities that look similar to chains, plates, or even clusters but limited to the short to medium range on the subnanometer scale in at least one of the three dimensions. The phase separation tendency is also confirmed by the calculated Warren-Cowley chemical short-range ordering parameter (CSRO) being between 0 and 1. The nearest neighbor coordination numbers around Ni and Ag presented in Fig. 4(a) suggest chemical intermixing but preference for like bonds over the statistical averages.

Enthalpy calculations provide an additional check to judge whether the simulated configuration is close to what is actually present. The enthalpy difference between the RMC model and the phase-separated state, calculated using molecular dynamics (MD) at 300 K with the embedded atom method potential [19,20], was 10 kJ/mol, in good agreement with that measured from heat of crystallization. Interestingly, direct MD simulations starting from either quenched liquid or unrelaxed fcc solid solutions at 300 K also yielded Ag-Ni alloys that are amorphous as indicated by their RDFs and stable for the duration of the MD runs. The enthalpy of the amorphous state again agrees with the measured value, and its structure [Fig. 4(b)], EXAFS, and CSRO parameter are all similar to those found in experiments [21]. The fact that all these happen even on MD time/size scales is a strong, additional proof, independent of the EXAFS data and RMC modeling, of our main points: Alloyed Ag-Ni is amorphous but quickly develops an ultrafine, partially decomposed nonuniform structure, leading directly to an anomolous enthalpy state that is considerably lower than not only that of an extrapolated liquid (possibly up to 30 kJ/mol according to one estimate [14]), but also that of an fcc Ag-Ni solid solution (+24 kJ/mol [21]). Because of space limitations, the Ag-Ni enthalpy-composition diagram will be discussed elsewhere [21].

In summary, we produced new Ag-Ni alloys through the highly nonequilibrium vapor quenching route. For a range of deposition parameters, the product phase appears to be clearly without long-range order, or "amorphous" as defined conventionally [1–9]. Such an alloy has apparently been able to sample phase/configuration space to some extent to lower its energy. The heat of crystallization is, similar to their $-\Delta H$ counterparts, down to $<\sim 10$ kJ/mol. However, very different from the normal $-\Delta H$ glasses, this kinetically trapped alloy is highly unusual and characterized by a nonuniform spinodal-like structure on the atomic level [Fig. 4(b)]. Such ultrafine heterogeneous structures develop because Ag and Ni have little affinity for each other even in the (undercooled) liquid state such that there is a strong tendency for the unstable alloy to decompose over a wide range of temperatures during quenching deep into the miscibility gap. The configuration [22] we have captured under the severe kinetic constraints is an inhomogeneous alloy rather than the energetically more favorable fully phase-separated state, which would otherwise quickly crystallize. The local structure was rarely seen in amorphous alloys previously and is difficult to classify conventionally, especially with respect to the degree of crystal-like order likely to be present on the short to intermediate range on subnanometer scale (Fig. 4). It is this nature of the atomic-scale structure that is directly and quantitatively responsible for the anomalously low heat of crystallization observed. The alloy enthalpy is even lower than the interpolated value ($+15$ kJ/mol) at $Ag_{40}Ni_{60}$ between the heats of fusion of pure Ag and Ni, thus exhibiting an apparent $-\Delta H$ [10]. Note, however, that the alloyed amorphous solid, with excess specific heat due to the local structures, cannot be regarded as a mixture of the elemental liquids directly extrapolated to low temperatures [21]. While the pure metals cannot be frozen to reach the amorphous solid state using our deposition method, the two-component alloy is able to escape crystallization into an elemental mixture due to the composition gradients developed after partial decomposition and the slower kinetics resulting from the coexistence of two intermixed species of different sizes and diffusivities. The amorphous alloy is metastable against crystal nucleation (Fig. 2). Upon heating, the presence of an unusually large number of quenched-in decomposition features with local short to medium range order and/or composition fluctuations already away from the nominal $Ag_{40}Ni_{60}$ renders the alloy well prepared for rapid crystallization as soon as the latter is kinetically possible, as reflected by the sharp crystallization peak at a fairly low temperature. We stress again that our combined results including the magnetic properties indicate that these structural features are *not* isolated, well-defined nanocrystalline elemental grains or clusters. Rather, they interconnect and spread out in a spinodal fashion in a true binary alloy [Fig. 4(b)] that is amorphous under all conventional, long-range probes. The degree of the development of such phase-separation features in other reported $+\Delta H$ alloys would depend on the magnitude of the $+\Delta H$ [3–9] (atomic size difference and electronic structures) and processing details including post deposition aging. We conclude that, in systems such as Ag-Ni with a strong liquid immiscibility, the amorphous alloys obtained are not the homogeneous, high-energy frozen liquids often assumed. While appearing the same as the $-\Delta H$ glasses, the nature of these $+\Delta H$ amorphous structures is nonuniform and spinodal-like on an extremely fine scale, leading directly to an energy reduction favorable for their appearance. An analysis of the local icosahedral ordering, which further confirms the amorphous nature of the structure and contributes to the lowering of its energy, will be presented elsewhere.

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[1] A. L. Greer, Science **267**, 1947 (1995).
[2] W. L. Johnson, Prog. Mater. Res. **30**, 81 (1986); MRS Bull. **24**, 42 (1999).
[3] S. Mader, H. Widmer, F. M. d'Heurle, and A. S. Nowick, Appl. Phys. Lett. **3**, 201 (1963).
[4] J. J. Hauser, Phys. Rev. B **12**, 5160 (1975).
[5] M. Nastasi, F. W. Saris, L. S. Hung, and J. W. Mayer, J. Appl. Phys. **58**, 3052 (1985).
[6] H. Rizzo, T. Zocco, T. B. Massalski, and M. Nastasi, Metall. Trans. A **24**, 1027 (1993); **25**, 1579 (1994).
[7] Y. G. Chen and B. X. Liu, Appl. Phys. Lett. **68**, 3096 (1996).
[8] B. M. Clemens and T. C. Hufnagel, Appl. Phys. Lett. **69**, 2938 (1996).
[9] K. W. Kwon, H.-J. Lee, and R. Sinclair, Appl. Phys. Lett. **75**, 935 (1999); Acta Mater. **47**, 3965 (1999).
[10] C. Michaelson, C. Gente, and R. Bormann, J. Appl. Phys. **81**, 6024 (1997).
[11] R. P. van Ingen, R. H. Fastenau, and E. J. Mittemeijer, Phys. Rev. Lett. **72**, 3116 (1994).
[12] H. G. Zolla and F. Spaepen, Acta. Mater. **47**, 2391 (1999).
[13] L. C. Chen and F. Spaepen, Nature (London) **336**, 366 (1988).
[14] A. R. Miedema, Philips Tech. Rev. **36**, 217 (1976); W. Luo and E. Ma, CALPHAD modeling work (unpublished).
[15] L. C. C. M. Nagamine, B. Mevel, B. Dieny, B. Rodmacq, J. R. Regnard, C. Revenant-Brizard, and I. Manzini, J. Magn. Magn. Mater. **195**, 437 (1999).
[16] A. Sadoc, Y. Calvayrac, A. Quivy, M. Harmelin, and A. M. Flank, J. Non-Cryst. Solids **65**, 109 (1984).
[17] S. J. Gurman and R. L. McGreevy, J. Phys. Condens. Matter **2**, 9463 (1990).
[18] Y. R. Wang, K. Q. Lu, and C. X. Li, Phys. Rev. Lett. **79**, 3664 (1997).
[19] V. Rasato and M. Celino, J. Appl. Phys. **86**, 6826 (1999).
[20] J. Cai and Y. Y. Ye, Phys. Rev. B **54**, 8398 (1996).
[21] J. He, H. Sheng, and E. Ma, Appl. Phys. Lett. **78**, 1343 (2001).
[22] W. Klein, H. Gould, R. A. Ramos, I. Clejan, and A. I. Mel'cuk, Physica (Amsterdam) **205A**, 738 (1994); A. I. Mel'cuk, R. A. Ramos, H. Gould, W. Klein, and R. D. Mountain, Phys. Rev. Lett. **75**, 2522 (1995).