Understanding Precursor Phenomena for the R-Phase Transformation in Ti-Ni-Based Alloys

Daisuke Shindo, Yasukazu Murakami, and Takuya Ohba

Abstract

Precursor phenomena are critical issues for martensitic transformations. In this article, we show recent progress in understanding precursor phenomena to the R-phase transformation, which is important for both fundamentals and applications. Structural modulation in the parent phase was intensively studied by means of detailed analyses of the weak diffuse scattering of electrons with the aid of recently developed energy-filtered transmission electron microscopy coupled with x-ray diffraction. A peculiar domain-like structure, which originates from static transverse atomic displacements in the parent phase, was discovered by virtue of these advanced methods. The characteristics of this structure (e.g., size, shape, and temperature-dependence), as well as its role in the subsequent R-phase transformation, are discussed.

Introduction

The cubic (parent phase) to trigonal transformation (called the R-phase transformation) in Ti-Ni-based alloys is important for both fundamental understanding and applications.[1] In fact, most of the practical applications of Ti-Ni shape-memory alloys use the R-phase transformation, since it exhibits a small temperature hysteresis, as small as 1–1.5 K (Figure 1). The R-phase transformation was first found by Dautovich and Purdy[2] and then was well characterized by Sandrock et al.[3] by the sharp increase of resistivity, as shown in Figure 1. Since the R-phase transformation occurs prior to another martensitic transformation to a monoclinic phase, it was previously called a premartensitic transformation or believed to be a distinct second-order transformation. However, it is now established that the R-phase transformation and the subsequent transformation to the monoclinic phase are two competing martensitic transformations of the first order.[4–7] Practically speaking, the R-phase transformation is realized if Ti-Ni alloys are subjected to work-hardening, precipitation-hardening, or the addition of a third element such as Fe or Al.[1] The last method seems most effective; with its use, the subsequent martensitic transformation to the monoclinic phase is markedly suppressed,[8] and hence the R phase is observed in a much wider temperature range near ambient temperature, as shown in Figure 1.

From a physical point of view, the presence of diffuse incommensurate reflections[5–7,9,10] and their correlation with the subsequent R-phase transformation are interesting and have been controversial for many years. (The temperature range in which the diffuse incommensurate reflections are observed will be discussed later.) Understanding these precursor phenomena (i.e., those above the transformation temperature R_s) is of vital importance not only for establishing the transformation mechanism, but also for developing further smart and stable shape-memory alloys in the future. This article presents recent findings on the precursor phenomena for the R-phase transformation obtained by detailed studies with newly developed advanced transmission electron microscopy (TEM)[11–13] and x-ray diffraction (XRD).[14,15]

Precursor Phenomena in Ti-Ni-Based Alloys

Since the R-phase transformation is of the first order, a prominent change in the crystal structure should take place below a definite transformation temperature R_s, which will be explained later. However, it has been pointed out that some structural changes occur even above R_s. They are detected by anomalies of elastic constants,[16] softening of a specific phonon branch (the TA_2 phonon),[17,18] and the appearance of incommensurate diffuse scattering.[5–7,9,10] Analyzing the diffuse scattering is a key approach to examining the characteristic features of the structural modulation, and in fact, many experimental and theoretical works have been done to date. Here, we briefly note the history and current status of exploration of the structural modulation above R_s. The most intensive and extensive studies may be those by Salamon and Wayman's group,[5,10] who carried out x-ray, electron, and neutron diffraction studies on Ti-Ni-Fe alloys in conjunction with measurements of resistivity, specific heat, and magnetic susceptibility. They have found that diffuse satellite reflections first appear at an incommensurate position, and then the incommensurability decreases with decreasing temperature until it locks into the commensurate state of the R phase. They accounted for these satellite reflections by a model involving discommensurations in the lattice strain, which were analogous to discommensurations in a charge-density-wave phase. Shapiro et al.[9] studied the incommensurate state using single-crystal XRD and reported that the incommensurability was neither regular nor periodic, that is, observed positions of satellite reflections depended on the Brillouin zone to which the reflections belong. Thus, they denied the possibility of the formation of a simple charge-density wave (a periodic, inhomogeneous density of electrons in a material) in the incommensurate state. To account for this peculiar incommensurability, Yamada[19] proposed a modulated lattice-relaxation