Superelastic Properties at Cryogenic Temperatures in Ti-Ni, Ni-Co-Mn-In and Cu-Al-Mn Shape Memory Alloys

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論文内容要約

Chapter 1: Introduction

Shape memory alloy (SMA) is a functional material that exhibits crystallographic change applications of temperature change, stress and magnetic field. Being totally different from common metals, SM undergoes such change without atomic diffusion, termed martensitic transformation (MT), during which t shape memory effect (SME) and the superelastic effect (SE) can be educed. By virtue of their exclusi functionalities, SME and SE have yielded huge opportunities for the design of applications. However, almost the applications of SME and SE are limited to Ti-Ni-based alloys exhibiting the R-phase transformation and to t narrow temperature window around the ambient environment. With respect to the study on low-temperatu applications, there have been fewer reports, especially below 77 K, in spite of their application potentialities in, f example, superconductive systems, next-generation fuels of liquefied gases, aerospace materials and cryogenic sealing materials. In addition, some anomalies in a cryogenic environment, such as the thermal transformation arrest (TTA) phenomenon in Ni-Mn-based metamagnetic SMA and the strain glass phenomenon in Ti-Ni-based SMAs, have been reported, attracting increasing interest from many researchers.

In this thesis, with an eye towards the low-temperature application of SMA and to clarify the fundamental curiosities about some reported anomalies in the low temperature region, Ni-Co-Mn-In, Cu-Al-Mn and Ti-Ni SMAs were selected and studied with regard to SE and/or SME behaviors, mainly at the cryogenic temperatures.

Chapter 2: Stress-Induced Martensitic Transformation at Low Temperatures in a $Ni_{45}Co_{5}Mn_{36}In_{14}$ Metamagnetic Shape Memory Alloy

In this chapter, stress-induced MT (SIT) behaviors in a $Ni_{45}Co_{5}Mn_{36}In_{14}$ alloy, which does not exhibit thermally-induced MT (TIT) down to the lowest temperature of 4.2 K, are presented in the temperature range of

4.2 - 200 K. At all the temperatures tested, almost perfect superelastic shape recovery was obtained and the critical stress for stress-induced transformation (σ_{Ms}) showed a concave temperature dependence in the forward transformation with decreasing temperature while that for reverse transformation (σ_{As}) monotonically decreased, resulting in a drastic increase of stress hysteresis (σ_{hys}) at low temperature. On the other hand, the equilibrium stress (σ_0), defined as the average of σ_{Ms} and σ_{As}, exhibited a tendency of temperature dependence decrement and converged to an almost constant value below ~150 K. The dissipation energy brought about by SIT, MFIT (magnetic-field induced MT) and TIT generally showed the same temperature dependence. This finding strikingly indicates that the driving forces to induce SIT, MFIT and TIT are equivalent and even that the total amount of excess energy for MT does not depend on the transformation route.

Chapter 3: Stress-Induced Martensitic Transformation at Low Temperatures in Cu-Al-Mn Shape Memory Alloys

In this chapter, three alloys, *i.e.*, Cu-17Al-15Mn and Cu-23Al-11,13Mn, which transform into 18R(6M) and 2H, respectively, were prepared. For Cu-17Al-15Mn, test specimens composed of different microstructures of single crystal, bamboo-like coarse grains (~2 mm in size) and fine grains (~200 μm in size) were examined to investigate the correlation between SE behavior and the density of the grain boundaries.

All the Cu-17Al-15Mn specimens showed SE down to the lowest temperature of 4.2 K and, especially in the single-crystalline sample, excellent superelastic properties, namely, small stress hysteresis and large superelastic strain of over 7%, were confirmed even at 4.2 K. On the other hand, the shape of the obtained stress-strain curve was considerably different for each sample and the flatness of the superelastic plateaus was lost in the fine-grained specimen because of the mixture of superelastic deformation and elastic deformation of the parent phase (and slip deformation at high temperature). In spite of such difference, the equilibrium stress exhibited a similar temperature dependence in all the samples tested, reflecting that the thermodynamical relationship of stability between the parent and martensite phases was, in principle, invariant to the change in the size of crystal grains.

With respect to the single-crystalline Cu-23Al-11,13Mn alloys, superelastic curves over a wide temperature range as well as a Cu-17Al-15Mn single crystal were obtained. In contrast to Cu-17Al-15Mn that maintained a significantly small σ_{hys} even at 4.2 K, σ_{hys} for the 2H martensitic transformation was considerably large and showed a linear increase with decreasing temperature.

Chapter 4: Stress-Induced Martensitic Transformation at Low Temperatures in a Ti-51.8Ni (at.%)

Shape Memory Alloy

In this chapter, polycrystalline Ti-51.8Ni alloy, possibly being in a strain glass state at cryogenic temperatures, was prepared. It exhibited SE with almost complete shape recovery in the temperature range from 40 to 180 K. While σ_0 showed a temperature dependence similar to that of Ni-Co-Mn-In, a dramatic increase in σ_{hys} was found at temperatures where the alloy was possibly in a strain glass state, being totally different in its magnitude from those of NiCoMnIn and CuAlMn alloys. In addition, a significant increase in σ_{Ms} on cooling enabled the occurrence of "heating-induced forward transformation" under a stress of 750 MPa from the parent phase supercooled down to 4.2 K without stress.

Chapter 5: Discussion on the Temperature Dependence of Equilibrium Stress Based on the Thermodynamic Theory

Since σ_0 gives the approximate equilibrium conditions, the use of the Clausius-Clapeyron relationship for σ_0 allows the estimation of the entropy change (ΔS) during SIT. Figure 1 shows a series of temperature dependence of ΔS of the alloys prepared in this thesis: NiCoMnIn, CuAlMn and TiNi alloys. Of great interest is that all the ΔS curves totally converged to zero when temperature approaching 0 K. This can be understood as a reasonable phenomenon obeying the third law of thermodynamics. In contrast, there was a significant difference in increasing behaviors of ΔS among these alloys. The origin of such difference is described by the temperature dependences of ΔS constituting components: vibrational entropy, $S_{vib.}$; magnetic entropy, $S_{mag.}$; and electronic entropy, $S_{el.}$. That is, for NiCoMnIn, the large contribution of $S_{mag.}$ in the parent phase and the abnormal relationship in Debye temperature of $\Theta_D^P > \Theta_D^M$ suppresses the increase in ΔS, allowing the occurrence of the TTA phenomenon. In contrast, for CuAlMn and TiNi alloys, the temperature dependences of ΔS are similar to the temperature dependences of $\Delta S_{vib.}$ with the estimated Debye temperatures of the parent and martensite phases.

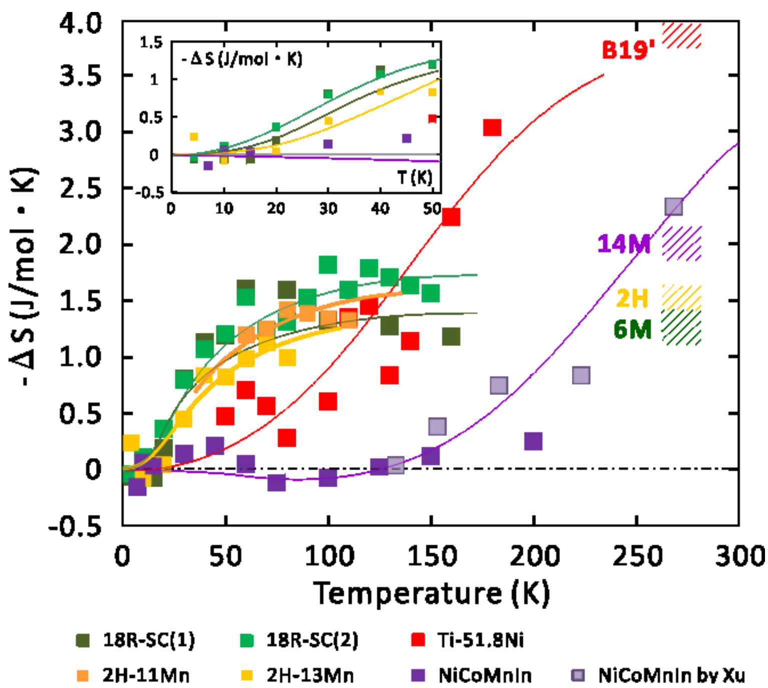

Fig. 1. Series of the temperature dependence of ΔS of the alloys prepared in this thesis.

Figure 2 shows a series of the temperature dependence of σ_{hys}. Larger σ_{hys} at lower temperatures introduces the occurrence of serration deformation, which brings about so-called cryogenic plasticity and yields larger latent heat during stress-induced transformation, being harmful for the surrounding low-temperature environment. In this chapter, a phenomenological understanding of the temperature dependence of σ_{hys} is offered and systematic investigations on the origin of the increase in σ_{hys} are made.

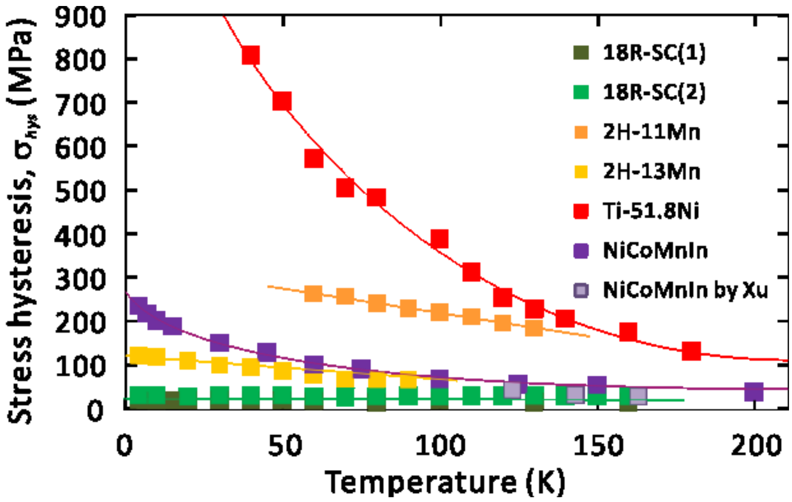

Fig. 2. Series of the temperature dependence of σ_{hys} of the alloys prepared in this thesis.

A phenomenological theory for the motion of habit planes was proposed by modifying Seeger's kinetic theory for CRSS of plastic deformation. The experimentally obtained σ_{hys} was successfully fitted using this proposed theory, and therefore, the origin of such increase was inferred to be due to the thermal activation process of the motion of habit planes. By the results of screening verifications, it was found that the magnitude and emperature dependency of the thermal activation component, σ_{TA}(T), were strongly dependent on the combination of crystal structures before and after transformation rather than on the kinds of obstacles possibly yielding energy barrier. Considering that the growth of martensite variant involves the creation of defects (mainly, dislocations) and that the compatibility of the lattice greatly affects the window of (thermal) hysteresis (although the latter is verified only at temperatures where the athermal component is dominant), it was tentatively proposed that the σ_{TA}(T) is uniquely determined by the amount and/or constituent of defects required to induce the martensitic transformation.

Chapter 7 Conclusions

In this chapter, the contents of chapters 1 through 6 are summarized.