Review paper

THERMODYNAMICAL ANALYSIS OF PSEUDOELASTICITY AND CALORIMETRY IN SHAPE MEMORY ALLOYS

Sei MIURA and Hiroyuki KATO

*Department of Engineering Physics and Mechanics, Faculty of Engineering,
Kyoto University, Kyoto 606-01, Japan*

Abstract: The relation between pseudoelastic behavior and the thermoelastic transformation has been studied by means of the measurements of stress-strain curves in the temperature range above and below the martensitic transition temperatures in so called shape memory alloys. Thermodynamical analysis for the pseudoelasticity associated with the stress-induced martensitic transformation has been briefly reviewed and in conjunction with the measurements of latent heat of transformation, the thermoelastic martensitic properties are discussed from a thermodynamic point of view. It was found that using the Clausius-Clapeyron equation concerning the stress-strain relation obtained by the experiments, the enthalpy change was calculated and agreed reasonably well with the experimental values. The importance of the measurement of latent heat of transformation was emphasized for the justification of thermodynamical analysis of the pseudoelasticity associated with the stress-induced martensitic transformation in the shape memory alloys.

Key word: *thermoelastic martensitic transformation, shape memory effect, pseudoelasticity, superelasticity, stress-strain curve, thermodynamics, Clausius-Clapeyron relation*

1 INTRODUCTION

Partly owing to the requisition for its engineering applications, large amount of investigations have been imposed on the shape memory effects in alloy in the last two decades. The shape memory effect is the phenomena which was found in the thermoelastic martensite alloys undergoing transformation from parent phase to martensite phase thermoelastically, when the alloys were cooled down below the martensitic transformation temperature M_f and deformed, thereafter heated above the reverse transformation temperatures A_f , the deformation is removed, thus the original shape is recovered.

Also, it was found that after the deformation was made at little higher than A_f temperature upon unloading the strains recovers to regain the original shape like rubber showing the elastic recovery. This phenomena is called as pseudoelasticity or superelasticity. These two phenomena are mutually related.

In order to understand the properties of shape memory alloys, we must know the essential features of the transformation behaviour under stress associated with the martensitic transformation. Therefore, it is necessary to perform the analysis of the stress-strain curves and their thermodynamical analysis.

The fundamental stress-strain curves are mainly classified to "Ferroelasticity" and "Pseudoelasticity or Superelasticity". The ferroelasticity is directly related to the shape memory effect. The latter pseudoelasticity is further divided into "Transformation pseudoelasticity" and "Twinning pseudoelasticity". As regard to the pseudoelasticity many reviews and articles have so far been reported in detail. Here, we will explain especially on the transformation pseudoelasticity associated with the stress induced martensite (SIM)

and its thermodynamical analysis and also the importance of the measurement of latent heat of transformation will be emphasized for the justification of thermodynamical analysis of pseudoelasticity in the shape memory alloys.

2 PSEUDOELASTIC LOOP AND FERROELASTIC LOOP

Here, we will explain the typical two types of stress-strain curves at above and below A_f point observed in the Au-47.5at.%Cd alloy single crystals.

When a single crystal of Au-47.5at.%Cd is under a tensile or compressive stress above A_f , such a double loop as shown in Fig.1 is observed. At point M, in the figure martensite is induced by stress and a jerky yielding is observed. When the stress is removed, the alloy is restored to the parent phase following a hysteresis loop. The different shape of the loop with tensile and compressive stresses comes from the different variants of the SIM's. This stress-strain behaviour was called a pseudoelasticity or superelasticity. This pseudoelasticity can be obtained between A_f and M_d , where M_d is the upper critical temperature that we can obtain for the stress-induced martensite without causing slip deformation. The critical stresses (M and M') increase with the testing temperatures between A_f and M_d .

On the other hand, in a thermal martensite phase (below M_f), hysteresis loops on the stress-strain curves of Au-47.5at.%Cd subject to repeat tensile and compressive stresses is shown in Fig.2. The loop for the first cycle is comparatively broad. The second and the following treatments result in guide the same loop, i.e. any work hardening is not observed. This loop was termed ferroelastic loop by present authors because it can be explained by analogy with the H-I curve of a

Fig. 1. Double hysteresis curves obtained by tension-compression test in the temperature range $A_f < T < M_d$ for Au-47.5at.%Cd (Superelastic loops)[1].

ferromagnet and the E-P curve of a ferroelastic material. Indeed, boundaries between twins of independent martensites are shown to move reversibly depending on an external tensile or compressive stress, and this is guide similar to, for example, motion of magnetic domain walls by an external magnetic field. The ferroelastic behaviour is missing above A_f and the sample is restored to its original shape, i.e. the shape memory effect. Plastic strain obtained below M_f is not due to the slip and, therefore, is not permanent. The deformation strain is, in other words, recoverable on the occasion of the transformation of martensite phase to the parent phase, and the original shape of the parent phase alloy is recovered.

Fig. 2. Tension-compression hysteresis loops below M_f for Au-47.5at.%Cd (Ferroelastic loops)[1].

The pseudoelastic loop above mentioned is associated with SIM above A_f . However, if a thermal martensite which shows a ferroelastic behaviour upon deformation is kept at room temperature and then examined, the stress-strain curve becomes superelastic and the critical stress increases with increase in the keeping time. This phenomenon is observed in Au-Cd, Au-Cu-Zn and Cu-Al-Ni alloys and this is called twinning pseudoelasticity.

3 THERMODYNAMICS OF TRANSFORMATION PSEUDOELASTICITY [7]

The relation between the chemical free energy of the martensite(M) and parent(P) phases of one component systems can be shown in Fig.3. Usually, the martensitic transformation occurs at the temperature where the driving force due to the free energy difference reached the same amount when supercooling has taken place below T_0 , equilibrium temperature where the free energy of parent phases (G^P) is equal to that of martensite phase (G^M). This temperature is so called M_s point where a martensite transformation starts. The driving force ΔG is expressed as follows:

$$\Delta G^{P \rightarrow M} = G^P - G^M = \Delta H^{P \rightarrow M} - T \cdot \Delta S^{P \rightarrow M} \quad (1)$$

where $\Delta H^{P \rightarrow M}$ is the enthalpy and $\Delta S^{P \rightarrow M}$ the entropy of transformation.

From Eq.(1), we obtain

$$\Delta H^{P \rightarrow M} = T_0 \cdot \Delta S^{P \rightarrow M} \quad (2)$$

where $\Delta G^{P \rightarrow M} = 0$, for the equilibrium temperature T_0 . Since $\Delta H^{P \rightarrow M}$ can be measured calorimetrically and T_0 can be obtained more or less accurately from the relations, $T_0 \simeq (M_s + A_s)/2 \simeq (M_f + A_f)/2$, where the M_s and M_f stand respectively for the starting and finishing temperature of the martensitic transformation on cooling and the A_s and A_f stand respectively that for the reverse transformation on heating. Then, we can obtain

$$\Delta S^{P \rightarrow M} = \frac{\Delta H^{P \rightarrow M}}{T_0} = \frac{d\Delta G^{P \rightarrow M}}{dT} \quad (3)$$

As $\Delta S^{P \rightarrow M}$ gives the rate of change of the free energy difference with deviation from T_0 it is an essential quantity with respect to the transformation behaviour with and without applied stress.

Assuming that the transformation occurs when the same amount of driving force as that of $\Delta G_{M_s}^{P \rightarrow M}$ at the M_s point by the aid of external stress at the temperature between M_s and T_0 , the work done on the stressed specimen is calculated on the basis of a uniaxial tensile or compressive applied stress which induces shear as well as volume stresses in the specimen.

This work is called the mechanical driving force for the martensitic transformation and the external work is written simply as the sum of the work done by shear stress τ and the normal stress acting on the shear plane σ ,

Fig. 3. Temperature dependence of the free energy G^P and G^M of a parent (P) and martensitic product (M) phase[7].

$$W = \tau \cdot \gamma_0 + \sigma \cdot \epsilon_0 \quad (4)$$

where ϵ_0 is the strain for the displacement along the normal to the shear plane, and γ_0 is the shear strain for the transformation along the shear direction [8].

The stress dependence of the free energy change is obtained from

$$W = \Delta G_{\sigma}^{P \rightarrow M} = \frac{1}{2} \sigma_a [\gamma_0 \sin 2\theta \pm \epsilon_0 (1 + \cos 2\theta)] \cdot V_m \quad (5)$$

where $\Delta G_{\sigma}^{P \rightarrow M}$ is the free energy difference under stress, σ_a the applied stress, θ the angle between the stress axis and the normal to the operative shear plane, and V_m the molar volume [8].

The maximum effect is obtained for the transformation shear system for which

$$\Delta G_{\sigma}^{P \rightarrow M} = 0 \quad (6)$$

From this, the condition for the direction of the applied stress to the shear system most prone to transformation is

$$\tan 2\theta = \pm \gamma_0 / \epsilon_0 \quad (7)$$

If we assume that $G(T)$ is a linear function and $\Delta G_{M_s}^{P \rightarrow M}$ is constant, we equate

$$\frac{d\Delta G_{\sigma}^{P \rightarrow M}}{dT} = \frac{d\Delta G^{P \rightarrow M}}{dT} = \frac{\Delta H^{P \rightarrow M}}{T_0} = \Delta S^{P \rightarrow M} \quad (8)$$

Also with

$$\frac{d\Delta G_{\sigma}^{P \rightarrow M}}{d\sigma_a} = \frac{1}{2} [\gamma_0 \sin 2\theta \pm \epsilon_0 (1 + \cos 2\theta)] \cdot V_m = \epsilon_M \quad (9)$$

where ϵ_M is the total strain tensor associated with the transformation, we obtain:

Fig. 4. Temperature dependence of the transformation free energy $G^{P \rightarrow M}$ and the influence of stress[7].

$$\begin{aligned} \frac{dT_0}{d\sigma_a} &= \frac{dT}{d\Delta G_{\sigma}^{P \rightarrow M}} \cdot \frac{d\Delta G_{\sigma}^{P \rightarrow M}}{d\sigma_a} \\ &= \frac{T_0}{\Delta H^{P \rightarrow M}} [\gamma_0 \sin 2\theta \pm \epsilon_0 (1 + \cos 2\theta)] \cdot V_m \\ &= \frac{\epsilon_M}{\Delta S^{P \rightarrow M}} \end{aligned} \quad (10)$$

Figure 4 illustrates the relation graphically. The curve of the free energy change accompanying the transformation $\Delta G^{P \rightarrow M}$ is displaced as a function of external stress. The magnitude of the displacement is inversely proportional to the transformation entropy such that, with reference to Table 1, the stress effects on some of the Cu- and Au- based alloys are expected to be considerably larger than on Fe-based alloy, if ϵ_M is assumed to be approximately equal.

A rough approximation of Eq.(10) may be obtained by using the relation

$$\frac{d\sigma_a^{P \rightarrow M}}{dT} = \frac{\rho \cdot \Delta H^{P \rightarrow M}}{\epsilon^{P \rightarrow M} \cdot T_0} \quad (11)$$

where $\sigma_a^{P \rightarrow M}$ is the applied stress at which stress induced martensite is formed at testing temperature T , ρ the density, and $\epsilon^{P \rightarrow M}$ the strain corresponding to complete transformation; $\sigma_a^{P \rightarrow M}$ and $\epsilon^{P \rightarrow M}$ are taken from the stress-strain curve. This equation is so called the Clausius-Clapeyron relationship. We will show that the values of $\Delta H^{P \rightarrow M}$ calculated from the stress strain curve and the measured values of the latent heat of transformation agree well within experimental accuracy from the results obtained by the present authors. The stress-induced martensitic transformation makes it possible thermodynamically to the transformation to M_1 martensite phase at lower stresses and M_2 martensite phase at higher stresses and this was actually found experimentally.

4 PSEUDOELASTICITY OF THERMOELASTIC MARTENSITE AND MEASURE-

Table 1. Typical thermodynamic data of martensitic transformations[7].

Alloy	$\Delta H_{T_0}^{P \rightarrow M}$ (J/mol)	T_0 (K)	$\Delta S^{P \rightarrow M}$ (J/mol)	$\Delta G_{M_s}^{P \rightarrow M}$ (J/mol)	$\Delta T(K)$ $= A_f - M_f$	Ref.
Au-Cd	281.1–410.0	330–350	0.8 ± 0.4	8 ± 0.4	20	(9)
	368–443	266–363	1.3 ± 0.4	–	–	(1)
AuCuZn	502–711	0–275	3.14 ± 1.05	15 ± 4	10–50	(10)
Cu-Al	167–272	300–800	0.33 ± 0.08	21 ± 8	40	(11)
Cu-Zn	314	0–300	1.1	13	48	(11)
Ti alloy	–	–	–	209–251	–	(12)
Fe-C	–	–	5.9	628–1883	–	
Fe-Ni	2510–2929	–	–	–	200–400	(13)
Fe-Cr	–	–	–	293–1464	–	

MENT OF LATENT HEAT OF TRASFORMATION

4.1 Au-Cd Alloys

As already shown in Fig.1, an Au-47.5at.%Cd single crystal exhibits pseudoelasticity (superelasticity) in the temperature range $A_f < T < M_d$, and the critical stress σ_M increases linearly with increasing temperature.

Direct observations of moving interfaces, which produce superelastic stress-strain loops, were made by optical microscope and X-ray diffraction on Au-47.5at.%Cd-0.7at.%Cu alloy deformed above T_0 . The addition of 0.7at.%Cu to Au-47.5at.%Cd decreases T_0 to about 6°C , when the sample has a β_1 (bcc) at a room temperature of 25°C . As shown in Fig.5, the superelasticity was obtained by tensile deformation at 25°C . When the critical stress for yielding was reached an interface appeared at an edge of the specimen and moved into another.

It is worthy of note that a lamellar band composed of alternate thin layers of β_1 (bcc) and SIM(β') appeared just behind this moving interfaces, disappearing further from this interface and thus a single oriented martensite resulted. It was confirmed that the crystal structure of the SIM was analyzed to be an orthorhombic structure (2H) with an axial ratio $a:b:c = 1:1.48:1.43$, and the lattice orientation relationship between the β phase and the SIM was $(011)_{bcc} // (001)_{orth}$, and $[\bar{1}\bar{1}1]_{bcc} // [\bar{1}\bar{1}0]_{orth}$, which was the same as that of the thermal martensite obtained by Chang and Read [15]. On removal of the stress, the interface moved back in the opposite direction and β_1 phase (bcc) was recovered with showing pseudoelasticity (superelasticity).

Stress-strain curves below T_0 that is M_f point are shown in Fig.6 [14]. Au-47.5at.%Cd alloy shows two

stage yielding below T_0 . The first stage yielding behaves as ferroelastic loop similar to Fig.2 and is associated with the movement of interface twin boundaries in the martensite. The second stage shows pseudoelasticity due to martensitic transformation to another SIM. On the other hand, in Au-49.5at.%Cd alloy, below T_0 , a significant pseudoelasticity was observed without leaving residual strain upon unloading and the critical yield stress increases with decreasing the temperature of deformation. In this alloy, a thermal hexagonal martensite β'' (trigonal crystal structure [16]) does not contain internal twins and it is shown that from the thermal martensite, the new martensite having different crystal structure was stress induced at the yielding point in the Fig.6(below).

In Fig.7 is shown this case of single crystal of Au-49.5at.%Cd alloy. As the M_s temperature exists at 30°C , the stress-strain curve obtained at 18°C signifies the fact that the thermally formed martensite (β'') was deformed by tension. Therefore, the stress-strain superelastic loop obtained is just the same as that obtained in Fig.5. It was evident from the microscopic observation that a new SIM appeared from the thermal β'' martensite, and the interface moved from one edge of the specimen to the other. Also in this case, a similar lamellar structure appeared just behind the moving interface, gradually disappearing further from the interface and finally a single crystal of SIM(β'_s) was obtained. Upon unloading, the reverse motion of the interface was observed. This SIM was, from the Laue pattern, confirmed as the β' structure. It is of importance that the martensite induced by tensile deformation has only the β' structure, regardless of the Cd content, while thermally produced martensite have different crystal structure, β' and β'' according to the Cd content.

As shown in Fig.1,2,5,6 and 7, the temperature de-

Fig. 5. Superelasticity and direct observation of the SIM formed in Au-47.5at.%Cd-0.7at.%Cu alloys at 25°C (i.e. below T_0) [14].

pendence of the critical stress was obtained below and above the transition temperature T_0 for single crystals of Au-Cd alloys containing five kinds of Cd contents from 46.5at.% to 50at.% and the result was shown in Fig.8. Here, σ_M and σ_Y are respectively the critical stresses for SIM and the yielding in the martensite, and σ_s is that for slipping. Both the curve made the minimum, but not zero, at about the M_s temperature, and the $d\sigma_M/dT$ represented almost constant in all the Cd composition range. The σ_Y increased with decreasing temperature below M_s in the 48.5at.%Cd or more, while in the 46.5 and 47.5at.%Cd, σ_Y maintained almost constant in all the Cd composition range. This is because in the case of ferroelastic loop as shown in Fig.2, the critical stress is almost unchanged with temperature as can be seen in Fig.6. Therefore, in the case of 48.5at.%Cd or more in which σ_Y increased with decreasing temperature, the temperature dependence of σ_Y corresponds to the case that SIM (β'_s) is newly formed from thermally formed β'' martensite, indicating the critical stress to induce martensite transformation increases with decreasing temperature.

From above results, the free energy-temperature diagrams for the Au-49.5at.%Cd are shown in Fig.9. Also the specimen containing the 48.5at.%Cd or more the thermal martensite β'' (trigonal) does not contain

Fig. 6. Stress-strain curves below T_0 in Au-47.5 and 49.5at.%Cd alloys[1].

twins in the internal structure, therefore, there is no movement of internal twin interfaces under stress and it is also consider that the interfaces of variants of martensite can not move, since the orientation relationship between the martensites is not that of twin relation.

From the Clausius-Clapeyron equation (Eq.(11)),

Fig. 7. Superelasticity and surface observation of the SIM in Au-49.5at.%Cd alloy at 18°C (i.e. below T_0)[14].

Fig. 8. Temperature variation of the critical stresses, σ_M and σ_Y , above and below T_0 , and σ_S for slip[1].

Fig. 9. Schematic free energy-temperature diagram for Au-49.5at.%Cd alloys. T_0 and T'_0 are almost equal[14].

by measuring the values of $d\sigma/dT$ and $\Delta\epsilon$, the amount of strain due to transformation, in the vicinity of the transformation temperature, the latent heat of the transformation $\beta(bcc) \rightarrow \beta'$ (orthorhombic) can be obtained above T_0 , whereas for the composition higher than 48.5at.%Cd, the latent heat of $\beta(bcc) \rightarrow \beta''$ (trigonal) can be calculated by adding the latent heat of transformation above and below T_0 . This is seen in Fig.9, i.e.

$$\Delta H_{T_0}^{\beta \rightarrow \beta''} = \Delta H_{T_0}^{\beta \rightarrow \beta'_s} - \Delta H_{T_0}^{\beta'' \rightarrow \beta'_s} \quad (12)$$

and the calculated values are in agreement with these measured by a scanning calorimeter as shown in Table 2.

It is interesting that the values for the latent heat of the transformation from β'' martensite to β'_s martensite are very small compared with those obtained in the $\beta \rightarrow \beta'$ and $\beta \rightarrow \beta''$ transformations.

4.2 Au-Cu-Zn Alloy

From a higher to a lower temperature, the β - $Au_{26}Cu_{74-x}Zn_x$ alloy have disordered bcc(β) phase, CsCl type ordered β_1 phase and the Heusler type ordered phase (H) at around the range $x \simeq 44$, and the martensite phase at a low temperature. This martensitic transformation is thermoelastic type, and its shape memory effect and the pseudoelasticity were reported in detail by the present author [17].

It is shown that the stress strain curves of β - $Au_{26}Cu_{26}Zn_{48}$ alloy single crystals in Fig.10, in which above the transformation temperature of the martensitic transformation T_0 , all curves behave as superelasticity associated with SIM. Below T_0 , all curves behaved as ferroelastic and for example, as shown by an arrow in Fig.10, the residual strains went back to zero when the specimen was heated up above the T_0 indicating the shape memory effect.

In Fig.11, it is shown the temperature dependence of the critical stresses of alloy single crystals for the compositions of $x = 45, 46, 47$ and 48 at.% which correspond to the electron-atom ratios (e/a) of 1.45, 1.46, 1.47, and 1.48. As shown in Table 3, the temperature obtained by extrapolating the critical stresses to zero stress correspond to T_0 (more precisely to M_s). The

Table 2. Calculated and measured latent heat of transformation in the Au-Cd alloys[14].

At.%Cd	$T > T_0$			$T < T_0$			Calculated	Measured
	$\Delta\epsilon$ (%)	$d\sigma/dT$ (MPa/K)	$\Delta H_{T_0}^{\beta \rightarrow \beta'}$ (J/mol)	$\Delta\epsilon$ (%)	$d\sigma/dT$ (MPa/K)	$\Delta H_{T_0}^{\beta'' \rightarrow \beta'}$ (J/mol)	ΔH_{T_0} (J/mol)	ΔH (J/mol)
46.5	3.4	2.94	420	0	0	0	420	—
47.5	3.8	2.45	357	0	0	0	357	370
48.5	3.5	2.35	286	4.3	-0.471	-71	357	—
49.5	3.6	2.55	315	4.3	-0.588	-88	403	—
50.0	3.5	2.35	286	5.4	-0.520	-97	382	420
51.0	—	—	—	—	—	—	—	420

 Fig. 10. Typical stress-strain curves obtained above and below T_0 in $Au_{26}Cu_{26}Zn_{48}$ alloy[17].

temperature coefficients of the critical stress $d\sigma_M/dT$, where σ_M is the critical stress to induce the martensite, above T_0 are found to be almost constant in all the values of e/a studied: $d\sigma_M/dT \approx 3.0 \text{ MPa/K}$. It is difficult to determine the precise values of transformation strain just after the completion of SIM from the pseudoelastic loops of this alloy, however the calculated values of ΔH_{T_0} using Eq.11 were found to be about $130 \sim 200 \text{ J/mol}$, which were almost in good agreement with the measured values of the latent heat of transformation shown in Table 3.

4.3 Au-Ag-Cd Alloys

The pseudoelastic behaviour of the $Au_{52.5-x}Ag_xCd_{47.5}$ pseudo-binary alloys were investigated in detail in order to study the effect of Ag substitution upon the pseudoelasticity and also that of two kinds of atomic ordering such as CsCl-type, (AuAg), Cd, and Heusler-type, Au, Ag, Cd, upon the martensitic transformation temperature and the related pseudoelasticity.[18] For an example, it is shown in Fig.12 that the stress-strain behaviour at above and below of transformation temperature and also the relation between the critical stress and the temperature in Fig.13. As

 Fig. 11. Temperature variation of critical stresses, σ_M and σ_Y , above and below T_0 [17].

shown in the figure, yieldings with two stages similar to those obtained in the $Au_{47.5}at.\%Cd$ binary alloys were observed in the temperature range below M_f point.

The first yielding stress was quite small and the second yielding stress was larger than the first. The second yielding is associated with the martensite to martensite transformation; this yielding could be recovered after producing a reversible loop upon removal of the applied stress. In the temperature range above A_f , the two stage yieldings were observed and this is also due to the martensite to martensite transformation similar to those above mentioned, and with increasing the temperature only the first yielding with narrow pseudoelastic loop was observed. It is clearly shown in the Fig.13 that two yield points with different critical stresses appeared. In this case, a large stress difference between the forward and reverse yielding stresses was observed in the second yielding. From these results, the Clausius-Clapeyron equation applied to the stress-induced martensitic transformation can be used to calculate the enthalpy (ΔH) and entropy (ΔS) changes and the results calculated can be compared with those obtained experimentally (ΔH_R

Table 3. Measured latent heat and T_0 in the Au-Cu-Zn Alloys.[17]

Alloys	Transformation heat ΔH (J/mol)	$T_0(^{\circ}\text{C})$ $(M_s + A_s)/2$
Au ₂₆ Cu ₂₉ Zn ₄₅	200±40	67±3
Au ₂₆ Cu ₂₈ Zn ₄₆	160±40	35±3
Au ₂₆ Cu ₂₇ Zn ₄₇	160±40	-3±3
Au ₂₆ Cu ₂₆ Zn ₄₈	155±40	-21±3

Fig. 12. Variation of stress-strain curves in Au-32.5at.%Ag-47.5at.%Cd alloys quenched from 823K to 273K[18].

Fig. 13. Critical stress-temperature curves in Au-32.5at.%Ag-47.5at.%Cd alloys quenched 823K to 273K[18].

and ΔS_R). The results are shown in Table 4 in which $T_0(K)$ is the temperature corresponding to zero stress for inducing martensite.

It is of interest to note that ΔH decreased with increasing Ag concentration, so that this tendency is quite similar to that of the change in T_0 against Ag concentration. Hence, the values of entropy change, ΔS , are almost constant, irrespective of Ag concentration. For example, $\Delta S \cong 1.0 \text{ Jmol}^{-1} \text{ K}^{-1}$ was calculated and good agreement is seen with the value obtained by Nakanishi *et al.* using differential scanning calorimetry[19].

On the other hand, some thermodynamical data related to the entropy change in martensitic transformation have been reported as shown in Table 1, except for the case of ferrous martensite ($\Delta S = 5.9 \text{ Jmol}^{-1} \text{ K}^{-1}$ for Fe-C alloy), the values are found to be in the range of $3.2 \sim 0.5 \text{ Jmol}^{-1} \text{ K}^{-1}$ in the β -phase alloys.

4.4 In-Tl Alloys

The stress-strain curves of In-Tl alloys associated with the thermoelastic martensitic transformation show following characteristics. As seen in Fig.14, above $M_s \cong 320\text{K}$ (22.0at.%Tl) and the low temperature region below 232K, superelastic loops were obtained. In the intermediate temperature region, removal of the stress left residual strain and the residual strain went back to zero when the specimen was heated to above the T_0 , showing shape memory effect. The superelasticity in the high temperature region is thought to be due to the reversible movement of the internal twin boundaries in the martensite phase, that is so far been called "rubber-like behaviour". In Fig.15 is shown the temperature dependence of critical yield stress. The temperature around 230K where the maximum stress obtained, appears to be independent of the Tl content, while the M_s point was largely dependent upon the Tl content [20,21,22].

From the superelastic loop due to SIM, ΔH obtained from Eq.11 was very small value as shown in Table 5, indicating the hysteresis is almost zero in this alloy. There have been reported few data on the heat of transformation of this alloy, except that $2.06 \pm 0.13 \text{ Jmol}^{-1}$ for In-20.5at.%Tl by Predel [24]. Patel and Ahmed [25] have made the calorimetric measurement on the alloys containing 16-21at.%Tl and obtained the values shown in Fig.16, however these

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Table 4. Latent heat and entropy values of the martensitic transformation calculated from the Clausius-Clapeyron equation and obtained experimentally in the $Au_{52.5-x}Ag_xCd_{47.5}$ pseudobinary alloy[18]. † Slowly cooled specimen

Ag (at.%)	$\Delta\epsilon$ (%)	$d\sigma/dT$ (MPa/K)	T_0 (K)	ΔH (J/mol)	ΔH_R (J/mol)	ΔS (J/mol · K)	ΔS_R (J/mol · K)
2.5	4.4†	2.1†	315†	314.6†	–	1.00†	–
	4.4	2.1	305	304.6	–	1.00	–
5.0	4.3	2.2	278	284.5	318	1.02	0.81
26.25	2.0	4.7	152	153.1	162	1.01	1.06
32.5	1.6†	3.5†	183†	109.6†	157†	0.60†	1.05†
	2.4	4.2	140	151.9	184	1.09	1.34
35	2.0	4.6	120	145.0	170	1.21	1.41
47.5	1.0	4.1	151	67.4	100	0.45	0.66

Table 5. Calculated latent heat of transformation in the In-Tl alloy single crystals[22].

At.%Tl	$\Delta\epsilon$ (%)	$d\sigma_M/dT \times 10^{-3}$ (MPa/K)	T_0 (K)	ΔH (J/mol)
21	0.95	25.0	333	1.25
22	0.95	23.0	311	1.08
23	0.55	19.0	290	0.50
24	0.61	12.6	230	0.29
26	0.63	78.8	211	1.67

Fig. 14. Variation of stress-strain curves with temperatures in In-22.0at.%Tl single crystal[20,21,22].

Fig. 15. Temperature variation of critical stress in In-21.0 - 26.0at.%Tl single crystals[22].

Fig.16. ΔH vs. alloy composition in In-Tl alloys(after Patel and Ahmed[25]).

values are very large.

As regard to this work, Bonte *et al.*[26] reported that the values of ΔH obtained by Patel and Ahmed may be due to the experimental error, considering the results by the present author. Reliable data has not so far been obtained owing to the extremely small value of the latent heat. Recently, careful measurement was made by the present authors by using differential scanning calorimeter and the results obtained are shown in Table 6, where ΔH is the latent heat of forward transformation and ΔH_R is that of reverse one [27]. These data will not be so much reliable due to extremely small value of latent, however, the values of obtained are $\frac{1}{20} \sim \frac{1}{30}$ of that obtained by Patel *et al.* and almost agrees with the values reported by Bonte, and also with the values shown in Table 5 calculated from stress-strain curves. Also it is to be noted that the transition temperatures obtained by the extrapolating the value of critical yield stress to zero (T_0 in Table 5) are in good agreement with the value of T_0 obtained by direct measurement as shown in Table 6.

4.5 Cu-Sn Alloys

It was first reported by Miura *et al.* that when the single crystal of β_1 phase near the composition of 15.0at.% Sn was quenched and deformed in β_1 phase, superelasticity due to SIM is observed and when the retained SIM was heated above A_f temperature, shape memory effect is observed [28]. The temperature hysteresis of transformation in the Cu-15.0at.%Sn alloy single crystal is very large almost reaches to 150K, showing an intermediate nature of thermoelastic and athermal martensites. Remarkable aging effect in the β_1 phase was also found, that is the decreasing of M_s temperature and the increasing of stress required for SIM. Detailed investigation on the aging effects has been developed in the literature [29].

Recently, a martensite to martensite transformation was confirmed by tensile test as shown in Fig.17, in which two-stage yielding was shown. The first and the second stage yield points corresponded to the initiation of the transformations, $\beta_1(D0_3) \rightarrow \beta'_1(18R)$ and $\beta'_1(18R) \rightarrow \alpha'_1(3R)$, respectively. Temperature variation of these critical stresses was shown in Fig.18.

Fig. 17. Stress-strain curve showing a two stage yieldings in the Cu-15.0at.%Sn alloy single crystal[29,30].

Fig. 18. Temperature variation of the critical stress in the Cu-15.0at.%Sn alloy single crystals[29,30].

The critical stress of the first yielding increased remarkably by an aging at 293K after quenching from 993K to 273K, but the second yielding stress did not change [29].

Measurement of the latent heat by DSC gives the transformation enthalpy of 140 J·mol^{-1} for the forward transformation. The estimation of this value from the critical stress and temperature relation can be made in principle through Eq.(11) as the same manner in another shape memory alloys. However, in the case of the CuSn alloy accompanying a large transformation hysteresis, a modification of Eq.(11) is necessary for the close estimation of the enthalpy change, since the contribution of the dissipative energy should not be negligibly small[28]. The following relation is deduced [30];

$$\Delta H^{\beta_1 \rightarrow \gamma'_1} = \left(T - \frac{A_s - M_s}{2} \right) \cdot \Delta S^{\beta_1 \rightarrow \gamma'_1} \quad (13)$$

where $\Delta S^{\beta_1 \rightarrow \gamma'_1}$ is the change in entropy, and can be estimated from the multistage transformation diagram of Fig.18. The M_s and A_s of the DSC sample

Table 6. Measured latent heat and T_0 in the In-Tl alloys [27].

Tl (at.%)	M_s (K)	M_f (K)	ΔH (J/mol)	A_s (K)	A_f (K)	ΔH_R (J/mol)	$T_0 =$ ($M_s + A_s$)/2
21	340.0	333.5	2.61	336.5	342.0	1.94	338
22	311.5	303.5	2.18	313.0	320.0	1.20	312
23	295.0	290.5	1.73	300.0	308.0	2.12	298
24	252.0	246.5	3.05	265.5	272.0	0.81	259
25	226.0	221.0	2.06	—	—	—	—
26	202.0	196.0	1.73	203.0	215.5	2.61	203

were determined from DSC curve as 135K and 240K. Then Eq.13 gives ΔH of 136 J mol^{-1} at the M_s , which agrees well with the measured value.

5 CONCLUDING REMARKS

The deformation behaviour of typical shape memory alloys; Au-Cd, Au-Cu-Zn, Au-Ag-Cd, In-Tl and Cu-Sn alloys is reviewed from a thermodynamical point of view. The temperature variations of stress-strain curves of these single crystals are categorized into ferroelasticity and pseudoelasticity (superelasticity) with respect to the equilibrium temperatures defined in the free energy diagram between parent and martensite phases. Thermodynamical analyses for pseudoelasticity are developed, and it is shown that from the temperature dependence of the yield stress for superelasticity, the latent heat of thermal transformation calculated by the Clausius-Clapeyron relation agrees well with that of directly measured by the differential scanning calorimeter. This fact will justify the thermodynamical equations for the thermoelastic martensitic transformation in shape memory alloys, developed in this study.

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