Effect of χ -Phase Precipitation on Elastic Modulus of Cu-Al-Ni-(Ti)-(Mn) Shape Memory Alloys

I. Hurtado, J. Van Humbeeck, P. Ratchev and L. Delaey

Department Metaalkunde en Toegepaste Materiaalkunde, Katholieke Universiteit Leuven,
W. de Croylaan 2, B-3001 Heverlee, Belgium

Cu-Al-Ni shape memory alloys present a minimum in their elastic modulus during the martensitic transformation, and the values in both the martensite and high temperature β -phase, follow the same trend. The addition of Ti, as grain refiner, produces χ -phase precipitates which substantially modify the elastic modulus profile of the alloy. The elastic modulus values of both martensite and β -phase increase to a different level, and no minimum during the transformation is observed. The specific changes in the elastic modulus depend upon the size distribution of the χ -phase precipitates, which, in turn, is a function of the thermomechanical history of the material. In the present article, a dislocation string model is used to qualitatively explain the elastic modulus profiles, making use of the coherency degree of the precipitates.

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I. Introduction

The mechanical properties of Cu-Al-Ni shape memory alloys are improved by the addition of elements such as titanium, as grain refiner, and manganese, replacing part of the Al. Ti forms precipitates, designated as the χ phase, which have a cubic Heusler type structure ($L2_1$) and a composition close to $(\text{Cu, Ni})_2\text{AlTi}^{(1)(2)}$. Based on its size and shape, two types of χ -phase precipitates have been distinguished in the Cu-Al-Ni-Ti alloys. The larger ones, few μm in size, are referred to as χ_L and do not have any defined shape. Others, with a size of several tenths of nm (≈ 45 nm), are the cuboidal χ_s precipitates. No strain contrast effect is reported around the χ_L precipitates, but a coffee bean contrast due to coherency strain has been verified around χ_s precipitates⁽¹⁾.

When Mn is added to the Cu-Al-Ni-Ti alloy, Ratchev *et al.*⁽³⁾⁽⁴⁾ denote the presence of particles smaller than 5 nm, which are not present in the Cu-Al-Ni-Ti material. In their work Ratchev *et al.* assumed that all the precipitates present in the alloy are χ -phase, $(\text{Cu, Ni})_2\text{AlTi}$, with a misfit parameter of +2.14% with respect to the β -phase.

The effect of the second phase precipitates on the martensitic transformation is manifold. Those precipitates affect the T_0 equilibrium temperature between the martensite and β phase because the chemical composition in the matrix changes. They also vary the additional undercooling, $\Delta T_m = T_0 - M_s$, necessary for the onset of the transformation⁽⁵⁾. This last effect is directly influenced by both the size distribution of the precipitates which vary the elastic limit of both martensite and high temperature β -phase.

Nakaniwa *et al.*⁽⁶⁾ and Sugimoto *et al.*⁽⁷⁾ have investigated the effect of the χ -phase precipitates on the internal

friction and elastic modulus of several Cu-Al-Ni-Ti-(Mn) alloys water quenched from high temperature. The behaviour of the elastic modulus is characterised by the following observations:

(a) The height of the internal friction peak associated with the martensitic transformation, measured at a frequency of 600 to 800 Hz with a heating/cooling rate of $2^\circ/\text{min}$, decreases sharply with increasing volume fraction of χ -phase. In contrast, the magnitude of the corresponding minimum in elastic modulus increases as the volume fraction of χ -phase increases. This result is explained by the decreasing mobility of interfaces between martensite and the parent phase due to grain boundaries as well as to the interaction of the martensite interfaces with the finely dispersed χ -phase particles.

(b) The elastic modulus of the martensite phase is reported to increase by the presence of χ -phase according to "a law of mixture". The interfaces between martensite and the χ -phase particles are not considered to contribute appreciably to the elastic modulus because the particles are incoherent.

(c) The elastic modulus of the parent phase is reported to be larger than the elastic modulus of the martensite. This behaviour is attributed to coherency, which causes "an elastically harder state at interfaces between the parent phase and χ -phase".

In this work, the effect of the three different χ -phase sizes on the elastic modulus of both β and martensite phases is analysed. Attention will be focused on the Cu-Al-Ni-Ti-Mn alloy (CANTiM), which shows a wider distribution in χ -phase size. The CANTi alloy, in which the small coherent precipitates are not present, will be used for comparison. Also a Cu-Al-Ni alloy without Ti, and consequently without χ -precipitates, will be used as reference and is denoted as CAN. In view of the results obtained in the present work, the results of Nakaniwa *et*

al.⁽⁶⁾ presented in the previous paragraphs will be further discussed and reinterpreted.

II. Experimental Procedure

Three Cu–Al–Ni–(Ti)–(Mn) alloys have been selected for the present investigation, Table 1. Their compositions correspond to martensitic transformation temperatures above 373 K. The grain refining effect of the Ti addition has been enhanced by extruding and hot rolling the material.

The results on the precipitate size were obtained using a JEOL-200CX transmission electron microscope (TEM) operating at 200 kV. Samples 1 mm thick were cut from the raw material either with a diamond blade saw in a low speed machine or by wire electro-erosion. Then they were heat treated and mechanically ground and polished to a thickness of about 0.15 to 0.2 mm. Discs of 3 mm diameter were cut from the thinned samples by spark erosion. The 3 mm diameter discs were further thinned to perforation by double jet electro-polishing. The electrolyte was a HNO₃–CH₃OH solution in a volume ratio 1/3, and the operation temperature –30°C. The voltage used varied from sample to sample depending on the type of structure and heat treatment, and also on the electrolyte flux rate. In general, good results were obtained in the range 8 to 10 V. All the measurements were performed at room temperature, and consequently the matrix was in the martensite state. The TEM techniques differ for the different precipitate sizes and are described elsewhere⁽⁸⁾.

Samples, 13 × 7 × 1 mm³, were cut from the as rolled material for Dynamic Mechanical Analysis (DMA) experiments and two kinds of basic heat treatment were performed for each of the CAN, CANTi and CANTiM alloys: The samples were brought into the β -phase state by holding at 1173 K for 1.8 ks and subsequently either air cooled or water quenched to room temperature.

Table 1 Overall composition of the alloys used in this work in mass%.

Composition mass%	Cu	Al	Ni	Ti	Mn	A_s^*/K
CANTiM	80.1	11.9	5.0	1.0	2.0	398
CANTi	82.6	13.4	3.0	1.0	—	473
CAN	83.0	13.0	4.0	—	—	393

*The initial retransformation temperature, A_s , has been measured after a heat treatment at 1173 K during 1.2 ks followed by a water quenching to room temperature.

Their elastic modulus was recorded using the bending resonant method. In the bending mode, the sample, in the form of a rectangular bar, is clamped rigidly at both ends and its central point vibrates sinusoidally by the drive clamp. The angular frequency, f , remains in the order of 10 to 50 Hz. The temperature is measured and controlled by a Chromel–Alumel thermocouple positioned immediately behind the sample. The scanned temperature range was between 223 and 493 K for the CAN and CANTiM alloys and 223 to 533 K for the CANTi, due to its higher transformation temperatures. The scanning rate was 5×10^{-2} K/s and the fixed amplitude 0.10 mm, which corresponds to a sample deformation of approximately $\epsilon \approx 2 \times 10^{-4}$.

Previous to the measurements, a full calibration of the apparatus constants and the response of the suspension were performed with standard materials. In DMA experiments the sample is mostly heated by air convection thus the heating rate should be kept low in order to allow the sample a linear and homogeneous increase in temperature. In the present measurements $T=3^\circ\text{C}/\text{min}$ has been found to be slow enough to allow homogeneity and fast enough to avoid stabilisation of the martensite or other ageing effects.

III. Results

1. Classification of the χ -phase precipitates in the CANTiM alloy

The χ -phase precipitates have been classified based on their size and shape, as well as on their calculated degree of coherence with the β -phase; this last criterion will become apparent when discussing the internal friction and elastic modulus measurements. Four types of precipitates could be distinguished. Their characteristics are reflected in Table 2, and in Fig. 1(a)–(d), where a representative TEM-micrograph of each type of precipitates is presented.

All the χ -phase precipitates, but the χ_{ss} due to their small size, have been identified as an intermetallic of approximate composition (EDAX) Cu_{0.25}Ni_{0.25}Al_{0.25}Ti_{0.25} and Heusler type structure. For this alloy, their distribution strongly depends upon the specific heat treatments. The influence of the heat treatments on the type of precipitates will now be described.

The conditions of the hot rolling and cooling have not been measured and consequently only an *a posteriori* description can be given (Table 3). The material is in the martensite condition at room temperature and no evi-

Table 2 Classification of all the possible χ -phase precipitates in the Cu–Al–Ni–Ti–Mn alloy.

CANTiM alloy	χ_L	χ_s	χ'_s	χ_{ss}
Diameter size	Several μm	50–150 nm	10 nm	3–5 nm
Shape	ovoid	cuboids	cuboids	ellipsoids
Coherence degree with the β phase	incoherent	semi-coherent	coherent?	coherent

Fig. 1 (a) χ_L precipitates in the Cu-Al-Ni-Ti-Mn alloy, (b) χ_s precipitates in a 1173 K air cooled Cu-Al-Ni-Ti sample, (c) χ'_s precipitates in a 1173 K water quenched Cu-Al-Ni-Ti-Mn sample, (d) χ_{ss} precipitates in a 1173 K air cooled Cu-Al-Ni-Ti-Mn sample.

Table 3 χ -phase distribution in the as hot rolled condition in the Cu-Al-Ni-Ti-Mn alloy.

χ_L	χ_s	χ'_s	χ_{ss}
Several μm	yes	yes	yes?

dence of other phases but martensite and χ -phases has been found. The χ_L precipitates remain without apparent change before and after performing all the heat treatments. Consequently their presence will not be further mentioned in the χ -phase distribution tables.

When the samples are water quenched from 1173 K, the smallest precipitates present in the sample, $\chi'_s \approx 10$ nm, are double the size of those obtained in the air cooled samples, $\chi_{ss} \approx 5$ nm. It is also observed that the mottled matrix[†] and the χ_{ss} precipitates, 3–5 nm in size, appear simultaneously and so do the 10 nm χ'_s precipitates and the coffee bean contrast. The effect of

[†] Mottled matrix and coffee bean contrast refer to the type of contrast observed by TEM⁽⁴⁾.

holding the sample in the β phase at 1173 K on the χ -phase distribution is presented in Table 4.

2. Classification of the χ -phase precipitates in the CANTi alloy

In contrast to the results from the CANTiM alloy, only three types of precipitates are observed in the CANTi alloy. Their characteristics are reflected in Tables 5 and 6. Another feature observed in this alloy is that as the size of the χ_s precipitates increases from 50 to 150 nm their shape changes from cuboidal towards a shape with protruded corners.

When the sample is air-cooled from 1173 K the smaller precipitates range from 10 to 20 nm, which corresponds to the χ'_s type in the classification. This type of precipitate does not appear if the sample is water-quenched, and the χ_s precipitates have a smaller size than in the air-cooled sample. In the case of the water-quenched sample, a mix of 18R and 2H structures is observed. For the air-cooled sample only the 18R structure is observed.

The present results confirm what is already known on the χ -phase precipitate distribution in Cu-Al-Ni-Ti al-

Table 4 Effect of the cooling rate on the χ -phase precipitates distribution in the Cu-Al-Ni-Ti-Mn alloy.

Heat treatment: 1173 K 1.8 ks and	χ_s	χ'_s	χ_{ss}	Remarks
air-cooled	150 nm	no	yes	mottled matrix contrast
or water-quenched	no	few, 10 nm	no	coffee bean contrast

Table 5 Classification of all the possible χ -phase precipitates in the Cu-Al-Ni-Ti alloy.

CANTi 1617A	χ_L	χ_s	χ'_s	χ_{ss}
Size	several μm	50–150 nm	10–20 nm	3–5 nm
Shape	ovoid	cuboid to octahedral	cuboid	not present
Coherence degree with the β phase	incoherent	semi-coherent	semi-coherent?	not present

Table 6 Effect of the cooling rate on the χ -phase precipitates distribution in the Cu-Al-Ni-Ti alloy.

Heat treatment: 1173 K 1.8 ks and	χ_s	χ'_s	χ_{ss}	Remarks
air-cooled	120 nm	yes	no	coffee bean contrast
or water-quenched	30–50 nm	no	no	distorted matrix β'' (lamellar mixture of 18R and 2H)

loys.⁽¹⁾⁽²⁾ The precipitates undergo a preferential growth along the cube diagonal directions as they lose coherency in the size range 50 to 150 nm. No mottled matrix contrast appears in this material, as the χ_{ss} precipitates, which give rise to such contrast, are absent for any treatment.

3. Elastic modulus measurements

The elastic modulus curves measured for the three alloys after either air cooling or water quenching from 1173 K are presented in Fig. 2. For simplicity, only a complete cycle is drawn in continuous which consists of the first cooling and second heating runs after the initial heat treatment. The elastic modulus in the martensite phase just after the initial heat treatment, without cycling, is represented by a discontinuous line.

The *CAN alloy* behaves as a typical shape memory alloy. The level of the elastic modulus for the martensite and β phases decreases as the temperature increases; during the martensitic transformation a clear minimum is observed, which is more pronounced for the water-quenched sample. The elastic modulus in the β phase for the air-cooled sample is higher than the one of the water-quenched sample.

In the *CANTi alloy* there is a sudden increase of the β elastic modulus after the transformation in the heating process both for the water-quenched and air-cooled samples, and there is not a deep minimum during the transformation. Comparing air-cooled and water-quenched samples, it can be observed that the main difference in elastic modulus between both treatments is related to the martensite phase. The modulus level of the water-quenched sample is lower than that of the air-cooled one.

In the *CANTiM alloy* there is not a clear minimum during the transformation, but the decremental trend of the modulus of martensite continues. In the air-cooled sample, a significant increment of the elastic modulus in the β phase is observed just after the first heating; it nearly doubles its value with respect to the martensite phase just before the transformation. As in the *CANTi alloy*, the evo-

Fig. 2 Elastic modulus curves for the Cu-Al-Ni, Cu-Al-Ni-Ti and Cu-Al-Ni-Ti-Mn alloys. The samples are water quenched and air cooled from 1173 K. The discontinuous lines correspond to the elastic modulus in martensite phase just after the initial heat treatment. The continuous lines correspond to a complete cycle, this is first cooling and second heating after the initial heat treatment.

lution of the elastic modulus is similar in both phases. In the martensite region, the level of the modulus during the first reverse transformation for the water-cooled sample

is much higher than that in the subsequent cycles.

Thus, the size and distribution of the χ precipitates play an important role in the level of the elastic modulus, both in martensite and β phase and also during the transformation. There is no minimum during the transformation and there is a large increment when the transformation finishes and the specimen becomes entirely β phase. It is also worth noticing that the elastic modulus of the martensite measured directly after quenching from 1173 K, is higher than the one obtained in the same sample after the second cooling from the β phase.

IV. Discussion

Very limited literature exists on internal friction measurements related to precipitation effects. Nevertheless special reference will be made to the recent results of Nakaniwa *et al.*⁽⁶⁾ already mentioned in the introduction. The current discussion will be mostly focused on the variation in the elastic modulus levels for the different alloys and treatments, principally with respect to the martensite and β phases.

The first point that needs clarification is the meaning of the elastic modulus which has been measured in the DMA. During this type of experiments the material is, ideally, deformed in the anelastic region. This means that the dislocations, and interfaces, present in the material are forced to bend between pinning points or even overcome shallow pinning points, depending on the applied stress. But the bending of the specimen proceeds until a position is reached from which the dislocations and interfaces move back to their equilibrium position when the stress direction is inverted.

Gerold⁽⁹⁾ reviewed the dislocation-precipitate interaction mechanisms operative in the range of our interest: two-phase alloys where the volume fraction of the second phase is of the order of 10^{-2} and in all cases less than 10^{-1} , and in addition, the second phase is assumed to be highly dispersed, i.e. the particle dimensions are in the range of 1 to 100 nm.

When a dislocation is moved by the applied stress along one of the slip planes of the matrix, it will encounter second-phase particles and interact with them. Depending on the nature of the second phase, and also on its crystallographic relationship with the matrix, different reactions may occur. Two limiting cases are possible:

(a) The particles are penetrable for the matrix dislocations, i.e. the particles will be sheared along with the matrix. This case can occur only under the special condition that the interface between the particle and the matrix is coherent. In the present measurements, the only case in which the precipitates seem to be fully coherent with the matrix is for the case of χ_{ss} precipitates in the β phase in the CANTiM alloy. Even this type of precipitate will be semicoherent in the martensite phase because of the difference in lattice parameters. Nevertheless, even in the most favourable case of complete coherency in the β phase, a strong elastic strain field exists around the χ_{ss} precipitates, and consequently the precipitates are not

expected to be sheared by the dislocations during the DMA experiments.

(b) The particles are non penetrable for the matrix dislocations, i.e. the particle will not be sheared along with the matrix by the dislocation movement in the matrix. In this case the dislocation is forced by the applied stress to bow around the particle. If the stress is large enough the dislocation will by-pass the particle leaving a dislocation loop around it which separates the sheared area of the matrix from the non sheared area of the particle. This is the well known Orowan mechanism which can be supposed to be the beginning of plastic deformation.

As already mentioned, during the DMA experiments, the material is being deformed in the anelastic regime. Consequently, the case in which the dislocations by-pass the particle and the Orowan loop is formed will not be considered, and the discussion will be restrained to the dislocation bowing. Thus having disregarded, in principle, the other mechanisms, the macroscopically measured elastic modulus will be explained as a function of the microscopic dislocation bowing. The measured elastic modulus is directly related to the square of the resonance frequency, ν_R , by means of factors which only depend on the sample geometry and on the inertia moment and spring constant of the arm suspension system, $E \propto \nu_R^2$. This measured frequency is built up from the microscopic resonant frequencies which, in a first approximation, can be directly related to the free dislocation between the obstacles which oppose their movement: $\nu \propto 1/l$, following the string model of Granato and Lücke⁽¹⁰⁾.

As this model seems to be more appropriate for the β phase where no interfaces exist and where the relations of coherency between the precipitates and the matrix seem more explicit, the discussion will be centred now on that phase. Afterwards, the model will have to be completed to explain the observations in the martensite phase and during the transformation.

The samples quenched from 1173 K have a higher concentration of pinning points, (specifically vacancies and Ti atoms in solid solution), a higher density of dislocations and a lower degree of order than the air cooled samples⁽¹¹⁾. The free dislocation length of the different samples can be, at least qualitatively, related to both the grain size and the amount of strong pinning points. The degree of order will have to be introduced as a correction to this approximation, since it will influence the facility of the dislocations both to glide and climb.

The average largest free dislocation length, l_g , is of the order of the mean grain diameter and these long dislocations will lead to a low resonant frequency ν_g . Also a similar frequency can be considered due to the grain boundary dislocations. These contributions will correspond to the lower limit of the frequency, which will be especially important for samples free of precipitates or samples in which the second phase particles are big and with a low population density.

In the CAN alloy, free of χ -phase precipitates, the

former contribution, ν_g , should be the most important, and consequently its β -phase modulus level be the lowest among the three alloys. This is only true for the water quenched sample. Searching for an explanation of the unexpected increase in elastic modulus of the air cooled sample, a careful TEM examination revealed the presence of small precipitates, probably γ -phase, in the martensite matrix. These precipitates present a coffee bean contrast in the martensite matrix; so they will be at least semicoherent. Consequently, the difference in elastic modulus level between the air cooled and water quenched samples in the CAN alloy should be related to the presence of these precipitates in the air cooled sample. The earlier justification for the smaller resonance frequency will thus be valid for the water quenched sample "devoid of precipitates". The air cooled sample behaviour will be discussed as compared with the samples containing χ -phase precipitates.

In the CANTi alloy the elastic modulus levels measured in the β -phase for both the water quenched and air cooled samples are similar (the air cooled one is slightly higher). This value is also similar to that of the air cooled CAN sample. This means that the presence of small semicoherent precipitates increases the elastic modulus.

Following the discussion on the different microstructural conditions leading to different frequencies in the material, the presence of semicoherent precipitates would have the effect of strongly pinning the dislocations, and consequently reducing the free length, $l_s < l_g$. The corresponding resonance frequency, ν_s , will thus be higher than that in the material free of precipitates, ν_g , and its effect will be an increase in macroscopic frequency, as it is indeed observed (Fig. 2).

The differences between the water quenched and air cooled CANTi alloy samples should be related to the different particle size distributions, i.e., size and/or volume fraction. The difference in size between the χ'_s and χ_s particles does not result in a drastic difference in their degree of coherency in the β phase; both of them have already lost coherency⁽⁸⁾. Hence, their effect in pinning the dislocations will be similar, and the differences measured will have to be attributed to different volume fractions of these precipitates. For a material similar in the amount of χ_s or χ'_s precipitates, the latter will be more numerous due to their smaller volume. Thus the contribution of the χ'_s to the measured macroscopic frequency will be larger than that of the χ_s precipitates and due to the smaller average distance among them, the frequency can even be expected to increase slightly, i.e. the resonance frequency due to χ'_s precipitates, ν'_s , is greater than that due to χ_s precipitates, ν_s . The combination of both effects explain the increase in the measured elastic modulus in the β phase in the samples with χ_s and χ'_s precipitates.

Among the elastic modulus values measured in the β phase, those of the CANTiM alloy, air cooled from 1173 K, are the highest (Fig. 2). For this alloy there is an additional variable in the form of χ_{ss} precipitates. These precipitates, are coherent with the β phase matrix and are

Fig. 3 Schematic view of the effective dislocation free length, l_{ss} , for the Cu-Al-Ni-Ti-Mn sample air-cooled from 1173 K.

surrounded by a strong elastic strain field⁽⁸⁾. Thus, the dislocations are not expected to interact directly with them, but with its strain field. In this case the mean effect of the χ_{ss} precipitates will be to make the dislocations either bend around them or cross slip. In the anelastic regime the former will be more probable. Thus, the effective dislocation length decreases to l_{ss} as is shown in Fig. 3. Because of the appreciable volume fraction of these precipitates, the contribution of the corresponding resonance frequency, denoted ν_{ss} , will be significant, producing the observed increase in elastic modulus of the CANTiM sample, air-cooled from 1173 K.

The increase in β -phase elastic modulus of the air cooled CAN alloy can then also be attributed to this type of interaction of the dislocations with small coherent precipitates. In the CAN alloy free of γ -phase precipitates (water quenched condition), the main frequency corresponds to a dislocation length l_g . This frequency is denoted ν_g . When the precipitates are present (air cooled sample) this length is effectively reduced by the interaction of the dislocations with the precipitates. In the air cooled CANTiM alloy, the main dislocation length is effectively reduced by the interaction with χ_{ss} precipitates. This length is denoted l_s and is smaller than the l_g .

At this point in the discussion, the model applied to explain the changes in the β -phase modulus will be extended to the martensite phase. This analysis is more complicated due to the large amount of variables which take part. First, there is the fact that the main contribution to the elastic modulus measured in the anelastic region is due to the movement of martensite-martensite interfaces in the material. The size and distribution of the martensite variants is strongly dependent on the thermomechanical history of the material. Moreover, TEM observations on the present samples have shown several features relating the type of χ -phase precipitates and the martensite variants formed around them. Although statistics are needed, there is a dependence of the χ size and degree of

coherency, on both the microstructure and state of defects of the martensite phase.

The χ_{ss} precipitates, assumed to be coherent and spherical in the β -phase, where they are formed, are distorted in the martensite phase due to the matrix distortion after transformation. Thus, although they are probably storing some elastic energy, some plastic deformation is produced mostly by means of a change in the stacking sequence⁽⁴⁾. The variants observed around these χ_{ss} precipitates belong to the same self-accommodating group.

On the other hand, around the cuboidal χ_s and χ'_s precipitates, apart from a certain change in the stacking sequence, the transformation stress field is mostly accommodated by the formation of new variants, even belonging to different self-accommodating groups. Thus, during the direct transformation, this is during cooling from beta to martensite, the growth of the plates stops at the precipitates and new plates nucleate around those precipitates.

Another feature, as explained by Ratchev *et al.*⁽⁴⁾, is the degree of coherency of the χ -phase particles in the martensite phase. Even the χ_{ss} precipitates have lost their coherency with the martensitic lattice, producing new stacking faults in the matrix, although this contribution of this structural change to the measured elastic modulus will be small compared with the one of the interfaces in the martensite. Consequently, one can expect that the overall increase in elastic modulus in the martensite phase is mostly due to the formation of new small groups of variants around the cuboidal χ_s and χ'_s precipitates. Following the simple vibrating model used for the β phase, the resonant frequency of the sample with small martensite plates should be higher than for one with big plates of martensite. This would increase the overall frequency measured. The fact that the precipitates increase the number of interfaces between variants not belonging to a self-accommodating group should also play a role in increasing the energy necessary to move them.

This model explains the high elastic modulus in the martensite for the CANTi and CANTiM alloys in which the semicoherent cuboidal χ -phase precipitates are present creating new martensite variants. It also explains why there are no changes in the CAN sample air cooled from 1173 K as compared to the water quenched one. Even though the former has precipitates, these do not alter the number or shape of the variants.

On the disappearance of the internal friction (IF) peak due to the transformation, models would become more complicated due to several contributions. In the first place, it should be reminded that the transformation peak during the IF measurements is due to the fact that cooling and heating rates are not zero. For an infinitesimal scan speed there would be a smooth sigmoidal-like curve joining the martensite and β phases. In the absence of precipitates, the modulus of β and martensite phases are approximately equal. Following the work of Stoiber⁽¹²⁾, the internal friction during the transformation depends not only on the amount of transformed mar-

Fig. 4 Scheme of the effect of the χ -phase precipitates on the elastic modulus in the vicinity of the martensitic transformation, after Nakaniwa *et al.*⁽⁶⁾

tensite, but also, through a factor, on the size of the variants formed. Consequently the new variants formed around the cuboidal precipitates could be responsible for the disappearance of the minimum, apart from the simple geometrical considerations of the different levels in elastic modulus among martensite and β phases. In the light of the previous discussion, the results of Nakaniwa *et al.*⁽⁶⁾ reported in the introduction, can be explained (Fig. 7). These authors consider that the increase in beta phase elastic modulus (region IV in Fig. 4) is due to “coherency, which causes an elastically harder state, at interfaces between parent phase and χ -phase”. To the contrary, the main contributors to the increase in elastic modulus measured in the anelastic region are not the small coherent precipitates, χ_{ss} , which were not observed by Nakaniwa *et al.*⁽⁶⁾ but the semicoherent cuboidal-like precipitates. On the other hand the contribution to the increase in martensite modulus (region III in Fig. 4) which was considered by Sugimoto⁽⁷⁾ as “increased by the presence of χ -phase according to the law of mixture”, is most probably due to the new variant arrangement around the cuboidal precipitates.

V. Conclusions

The semicoherent cuboidal-like χ -phase precipitates are the main contributors to the measured increase in elastic modulus in the β -phase. Their effect may be qualitatively understood with a dislocation string model in which the semicoherent precipitates act as pinning points. The small precipitates, coherent with the β -phase, would have the effect of opposing the dislocation movements, increasing the elastic modulus.

In the martensite phase, the contribution to the increase in martensite modulus is attributed to the new

variant arrangement around the precipitates.

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