A Detailed Observation on Successive Stress-Induced Martensitic Transformations in Cu-Al-Ni Alloy Single Crystals above A_f *

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A detailed observation on the successive stress-induced martensitic transformations in Cu-Al-Ni alloy single crystals has been carried out to clarify ambiguous problems left in a previous work (Acta Met., 27 (1979), 585). As a result, the structural change associated with two stage transformation pseudoelasticity above A_f has been revealed to differ depending upon the temperature range. In the temperature range between A_f and T_c (a critical temperature), distinct $\beta_1 \rightarrow \beta'_1$ and $\beta'_1 \rightarrow \alpha'_1$ transformations successively take place on loading, and distinct $\alpha'_1 \rightarrow \beta'_1$ and $\beta'_1 \rightarrow \beta_1$ reverse transformations do on unloading. In the temperature range above T_c , the transformation behavior of loading is the same as that in the temperature range between A_f and T_c . However, on unloading, when the loading has been stopped on the halfway of the second stage, the $\beta'_1 \rightarrow \beta_1$ and continuous $\alpha'_1 \rightarrow \beta'_1 \rightarrow \beta_1$ transformations successively take place. On the other hand, when the loading has been continued until the $\beta'_1 \rightarrow \alpha'_1$ transformation is completed, the associated stress-strain curve on unloading has clearly showed one stage of the continuous $\alpha'_1 \rightarrow \beta'_1 \rightarrow \beta_1$ reverse transformations. On the basis of these observations, the previous interpretation for the unloading process of stress-strain curves above T_c has been corrected, and the critical stress vs temperature diagram has been replotted.

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I. Introduction

An extensive study was previously made on successive stress-induced martensitic transformations and associated transformation pseudoelasticity in single crystals of Cu-Al-Ni alloys above and below $M_s^{(1)}$. The study revealed crystal structures of the stress-induced martensites, the nature of the stress-strain (s-s) behavior at each temperature range, the mechanism of the martensite-to-martensite transformations and a phase diagram in temperature-stress coordinates etc. However, some ambiguity has been left over on the transformation behavior at a temperature

range above A_f , because neither macroscopic nor microscopic observation of transformation process could be done owing to the elevated temperature.

The ambiguous problems can be specified as follows. In the temperature range between A_f and T_c (a critical temperature), the s-s curves showed two stage yielding both on loading and unloading (Fig. 3(e) and (f) in Ref. (1))[†]. This two stage pseudoelasticity was ascribed to two distinct stress-induced transformations, $\beta_1 \rightarrow \beta'_1$ and $\beta'_1 \rightarrow \alpha'_1$, on loading and their reversions, $\alpha'_1 \rightarrow \beta'_1$ and $\beta'_1 \rightarrow \beta_1$, on unloading. On the other hand, in the temperature range a little higher than T_c , the s-s curve showed only one stage on unloading, although two stages appeared on loading (Fig. 3(g) in Ref. (1)). The two stages on loading were similarly interpreted to the case in the temperature range between A_f and T_c , and the one stage on

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[†] The s-s curves of Fig. 3(e) to (h) in Ref. (1) will be shown later in Fig. 6(a) to (d), respectively, because the previous interpretation will be corrected.

unloading to be due to a continuous reverse transformation, $\alpha'_1 \rightarrow \beta'_1 \rightarrow \beta_1$. This interpretation of the unloading process is apparently consistent with the critical stress vs temperature plot in Fig. 7 of Ref. (1). However, no direct observation was made to evidence it in the previous work.

Furthermore, at still higher temperatures, the s-s curve showed indistinct two stages on unloading (Fig. 3(h) in Ref. (1)). This is inconsistent with the previous critical stress vs temperature plot, and no interpretation was given for the inconsistent point. Therefore, the present study has been conducted to straighten out these ambiguous problems by directly observing the transformation processes, using a small tensile device improved for observations at elevated temperatures. On the basis of the observations, some errors in the previous paper have been corrected.

II. Experimental Procedures

Two Cu-Al-Ni alloy single crystal specimens have been used in the present study, which are D1 used in the previous study and E1 newly formed. The orientations of both the specimens are very close to [001]. Their chemical compositions and transformation temperatures are shown in Table 1.

D1 specimen was used for optical microscopy observations of transformation processes during deformation. The observations have been performed at elevated temperatures using a small tensile device immersed in a silicon oil bath to avoid the oxidation of the specimen, the loading being stopped on the halfway of the second stage, since the previous s-s curves were taken in this manner to avoid

the risk of failure at an extraordinary large strain.

E1 specimen was used for a deformation experiment to obtain a more explicit s-s curve than in the previous study, and so it was deformed until the $\beta'_1 \rightarrow \alpha'_1$ transformation on the second stage was completed. The final heat treatment for E1 specimen was as follows:

1273 K for 300 s → Quenched into NaOH solution at 253 K.

The method of specimen preparation, single crystal production and others is almost the same as that in the previous study.

III. Results and Discussion

1. Morphological change in temperature range between A_f and T_c

Figure 1 shows microscopic morphological change when D1 specimen has been tensile-tested at about 390 K, a temperature between A_f (349 K) and T_c (425 K), and the associated s-s curve exhibits distinct two stages both on loading and unloading. The tensile direction is horizontal and the arrow in each photograph is a fiducial marker. By applying stress to the uniform β_1 matrix of (a), parallel plates of the β'_1 martensite with the $(1\bar{5}5)_{\beta_1}$ habit plane are stress-induced on the first stage of s-s curve, as seen in (b). With increasing strain, these plates coalesce into a uniform single region of the β'_1 martensite, (c). With further increasing stress, thin plates of the α'_1 martensite are then stress-induced in the β'_1 martensite on the second stage of s-s curve, (d). The habit plane of the α'_1 martensite is clearly different from that for the $\beta_1 \rightarrow \beta'_1$ transformation, and has been found to be the common basal plane of both the martensites, i.e., $(001)_{\beta'_1 \text{ or } \alpha'_1}$. With further increasing strain, these thin plates again coalesce into a single region of the α'_1 martensite, (e)[†].

When the stress is decreased, thin plates of the β'_1 martensite appear in the α'_1 martensite. The habit plane in this reverse transformation is the same as that for the $\beta'_1 \rightarrow \alpha'_1$ transforma-

Table 1 Chemical compositions and characteristic temperatures of the specimens used.

Sp.	Chemical composition (mass %)			Characteristic temperature (K)			
	Cu	Al	Ni	M_s	M_f	A_s	A_f
D1	bal.	14.0	4.2	308	296	306	349
E1	bal.	14.1	4.2	276	#	275	#

not measured

[†] However, the entire specimen does not become a single crystal of the α'_1 martensite as will be seen in Fig. 2.

Fig. 1 Microstructural change associated with the two stage transformation pseudoelasticity at 390 K, a temperature between A_f and T_c (Sp. D1). (a) to (e) correspond to loading process and (f) to (j) to unloading process.

tion on loading, as seen in (f) and (g)^{††}. Then, the specimen becomes a single crystal of the β'_1 martensite. However, no photograph showing the uniform single region of the β'_1 martensite was unfortunately able to be taken. On continued unloading, thin plates of the β_1 matrix appear in the β'_1 martensite exhibiting the same habit plane as that for the $\beta_1 \rightarrow \beta'_1$ transformation on loading, (h) and (i). When the stress is perfectly removed, the specimen regains a state of a single crystal of the β_1 matrix, (j).

Macroscopic morphological change has also been observed, and is shown in Fig. 2. Starting with a single crystal of the β_1 matrix shown in (a), the $\beta_1 \rightarrow \beta'_1$ transformation proceeds like a Lüders band on a macroscopic scale, (b) to (d). This behavior seems to contradict the microstructure of Fig. 1(b). Moreover, the up-

per and lower interfaces of the transformed region are, strangely enough, not parallel. To clarify these points, the upper interface portion of the transformed region has been observed over the specimen width under an optical microscope, and is shown in Fig. 3. The upper and lower regions are the β_1 matrix and the β'_1 martensite, respectively. It is to be noted that a wedge shaped transition zone exists between the two regions. In the β'_1 martensite region, however, several plates of the β_1 matrix are seen to remain untransformed. The upper boarder of the wedge shaped zone is the habit plane of the β'_1 martensite. On the other hand, the lower boarder of the zone is a secondary interface, which results from the fact that many β'_1 martensite plates with tapered boundaries merge into the large β'_1 martensite region. A similar secondary interface was also observed in a Cu-Zn alloy⁽²⁾. Only the upper of the two boarders of the wedge shaped zone is macroscopically visible as the upper interface of the transformed region of Fig. 2(b) to (d) in

^{††} Some obscure traces parallel to the habit plane in the $\beta_1 \rightarrow \beta'_1$ transformation are seen in (f) to (j). This is probably caused by the oxidation of the specimen, although the deformation has been performed in a silicon oil bath.

Fig. 2 Macrostructural change associated with the two stage transformation pseudoelasticity at 380 K, a temperature between A_f and T_c (Sp. D1). (a) to (h) correspond to loading process and (i) to (p) to unloading process.

Fig. 3 Microstructure of a portion near the upper interface of the band seen in Fig. 2(c).

a certain illumination condition.

A similar wedge shaped transition zone is observed in the lower interface portion of the transformed region. In this case, the lower boarder is also a secondary interface, but it results from the fact that many β_1 matrix plates merge into the large β_1 matrix region, and only this boarder is macroscopically visible as the lower interface of the transformed region. Accordingly, the upper and lower interfaces of the transformed region with visible contrast are not parallel. Figure 1(b) corresponds to a part inside the wedge shaped zone in Fig. 3, and thus no inconsistency exists between Fig. 2(b) to (d) and Fig. 1(b). The wedge shaped transition zone is formed, because an accommodation effect of the grip constraint occurs by allowing the transformed region to rotate. This $\beta_1 \rightarrow \beta'_1$ transformation behavior is somewhat different from the previously reported one in which the β'_1 martensite plates were nucleated from place to place extending over the entire specimen⁽³⁾.

Returning to Fig. 2, when strain is increased, the specimen becomes a single crystal of the β'_1 martensite, (e). Upon continued loading, the $\beta'_1 \rightarrow \alpha'_1$ transformation on the second stage proceeds like a Lüders band in the same way on the first stage, (f) and (g). However, the loading has been stopped, (h), before the entire specimen undergoes the transformation, because of the reason previously mentioned.

When the stress is decreased from this state, the α'_1 martensite first shrinks to revert to the β'_1 martensite, (i) to (k), and the specimen becomes a single crystal of the β'_1 martensite, (h). With further decreasing stress, the β'_1 martensite then shrinks, (m) to (o), and the specimen regains the β_1 matrix single crystal, (p). The above reverse transformation sequence of the $\alpha'_1 \rightarrow \beta'_1$ followed by the $\beta'_1 \rightarrow \beta_1$ indicates that the critical stress for the former transformation ($\sigma_{\alpha'_1 \rightarrow \beta'_1}$) is higher than that for the latter transformation ($\sigma_{\beta'_1 \rightarrow \beta_1}$) in this temperature range.

2. Morphological change in the temperature range above T_c

Figure 4 shows macroscopic morphological change when D1 specimen has again been ten-

Fig. 4 Macrostructural change associated with the two stages transformation pseudoelasticity at 430 K, a temperature above T_c (Sp. D1). (a) to (e) correspond to loading process and (i) to (p) to unloading process.

sile-deformed at about 430 K, a temperature above T_c , and the associated s-s curve has revealed two stages on loading and one stage or indistinct two stages on unloading. The transformation behavior on loading, (a) to (h), is the same as that shown in Fig. 2, but that on unloading is different. That is, the β'_1 martensite, not the α'_1 martensite, at both the end portions of the specimen first transforms back to the β_1 matrix, (i). As the $\beta'_1 \rightarrow \beta_1$ reverse transformation proceeds, the β'_1/β_1 interfaces approach the α'_1/β'_1 interfaces, (j), and finally encounter them. (k). Thereafter, the reverse transformation proceeds by movement of the composite interfaces of $\alpha'_1/\beta'_1/\beta_1$, (l) to (o). That is, as soon as the α'_1 martensite transforms back to the β'_1 martensite, the β'_1 martensite transforms back to the β_1 matrix. When this continuous reverse transformations of $\alpha'_1 \rightarrow \beta'_1 \rightarrow \beta_1$ are completed, the specimen regains the β_1 matrix, (p). The reverse transformation sequence of the $\beta'_1 \rightarrow \beta_1$ prior to the $\alpha'_1 \rightarrow \beta'_1$ ($\rightarrow \beta_1$) indicates that $\sigma_{\beta'_1 \rightarrow \beta_1}$ is higher

than $\sigma_{\alpha'_1 \rightarrow \beta'_1}$ in the temperature range above T_c . A similar reverse transformation sequence was also observed in a Cu-Zn-Al alloy⁽⁴⁾.

The composite interface of $\alpha'_1/\beta'_1/\beta_1$ has been observed microscopically, and is shown in Fig. 5. The upper and lower regions are the α'_1 martensite and the β_1 matrix, respectively. It is seen that the α'_1/β'_1 interfaces and the β'_1/β_1 interfaces are crossing each other. This can be

Fig. 5 Microstructure of the composite interface of $\alpha'_1/\beta'_1/\beta_1$ (Sp. D1).

also seen in Fig. 4(n) and (o). As a result, the α'_1 martensite plates with the $(001)_{\beta'_1}$ habit plane protrude into the β_1 matrix region, and the β'_1 martensite plates with the $(\bar{1}\bar{5}5)_{\beta_1}$ habit plane penetrate into the α'_1 martensite region. That is, the α'_1 martensite adjoins the β_1 matrix with the $(001)_{\beta'_1}$ plane, and the β'_1 martensite adjoins the α'_1 martensite with the $(\bar{1}\bar{5}5)_{\beta_1}$ plane. These are not expected from a calculation based on the phenomenological theory for martensitic transformation⁽³⁾. In a Cu-Zn-Al alloy, a similar crossing structure was observed associated with the stress-drop type s-s curve, and explained to be the one of two variants of β'_1 martensite with one variant of α'_1 martensite⁽⁴⁾⁽⁵⁾. Therefore, the crossing structure in Fig. 5 may be probably explained in the same way as that in a previous Cu-Zn-Al alloy. However, no X-ray Laue photograph, which proves that the thin plates protruded into the β_1 matrix showing $(001)_{\beta'_1}$ habit trace are the β'_1 martensite, has unfortunately been taken owing to difficulty of the experiment at elevated temperature. At any rate, a more detailed study is needed on this phenomenon.

3. Corrected interpretation for s-s curves

The s-s curves for D1 specimen tensile-deformed above A_f are again shown in Fig. 6. As described in the previous section, when the loading in the temperature range above T_c has been stopped on the halfway of the second stage, the β'_1 martensite, which has not transformed to the α'_1 martensite on loading,

Fig. 6 Stress-strain curves of Sp. D1 above A_f as a function of temperature (strain rate: 5.0×10^{-4} /s).

has first transformed back to the β_1 matrix and then the continuous $\alpha'_1 \rightarrow \beta'_1 \rightarrow \beta_1$ reverse transformations have occurred on unloading. Therefore, the interpretation for the unloading process of the s-s curves above T_c , (c) and (d), must be corrected as indicated in each s-s curve. The one stage with a gentle slope is seen on unloading in curve (c), because $\sigma_{\beta'_1 \rightarrow \beta_1}$ is slightly higher than $\sigma_{\alpha'_1 \rightarrow \beta'_1}$ at 444.5 K, and the indistinct two stages are seen on unloading in curve (d), because the former becomes much higher than the latter at 477.5 K. However, there is no necessity for changing the interpretation for the s-s curves, (a) and (b), in the temperature range between A_f and T_c .

From the above interpretation, only one stage is expected to appear on unloading at a temperature above T_c when loaded until the end of the second stage. To confirm this, another E1 specimen has been tensile-deformed, and Fig. 7 shows the s-s curve obtained at 423 K (23 K higher than T_c). As is expected, it shows only one stage on unloading. That is, the continuous $\alpha'_1 \rightarrow \beta'_1 \rightarrow \beta_1$ transformations only take place. Therefore, the stage begins to appear at a lower stress than that when the loading has been stopped on the halfway of the second stage.

The elongation associated with the $\beta'_1 \rightarrow \alpha'_1$ transformation is as large as 14.5%. This value of elongation is larger than the theoretically calculated 11%, and the reason for such a discrepancy is not clear at present.

4. Corrected critical stress vs temperature plot

From the above description, it is seen that

Fig. 7 Stress-strain curve of Sp. E1 at 423 K (above T_c) when deformed until the $\beta'_1 \rightarrow \alpha'_1$ transformation is completed (strain rate: 8.3×10^{-3} /s).

Fig. 8 Corrected definition of critical stresses when the loading is stopped on the halfway of the second stage.

$\sigma_{\alpha'_1 \rightarrow \beta'_1}$ and $\sigma_{\beta'_1 \rightarrow \beta_1}$ should be defined as shown in Fig. 8 instead of Fig. 6(c) in Ref. (1), when the loading was stopped on the halfway of the second stage. Using this definition, the critical stresses have been replotted against temperature, and Fig. 9 is the result obtained for D1 specimen. The $\sigma_{\alpha'_1 \rightarrow \beta'_1}$ has a linear relationship with temperature, being different from the previous one (Fig. 7 in Ref. (1)). This is quite reasonable, because no special reason exists why the stress hysteresis associated with the $\beta'_1 \rightleftharpoons \alpha'_1$ transformations drastically decreases in the temperature range above T_c .

In Fig. 9, the critical stress for the $\beta'_1 \rightarrow \alpha'_1$ transformation ($\sigma_{\beta'_1 \rightarrow \alpha'_1}$) increases with increasing temperature above 470 K. The reason for this is recently found to be due to an ageing effect occurring in specimens during tensile tests in this temperature range⁽⁶⁾. The increase of $\sigma_{\beta'_1 \rightarrow \alpha'_1}$ was formerly explained in such a way that no mechanism is available for direct

Fig. 9 Corrected critical stress vs temperature plot for each transformation indicated.

transformation of the β_1 matrix into the α'_1 martensite⁽¹⁾. However, this explanation is incorrect, because one stage continuous $\beta_1 \rightarrow \beta'_1 \rightarrow \alpha'_1$ transformations have also been found recently on loading of a specimen with a slightly different composition⁽⁷⁾. The transformations have been observed below 470 K, a temperature where no ageing effect is expected to occur. The morphology similar to the crossing structure in a Cu-Zn-Al⁽⁴⁾⁽⁵⁾ is expected to appear associated with the transformations. Investigation into the transformations is now in progress and details of the recent study will be published elsewhere.

IV. Conclusion

(1) In the temperature range between A_f and T_c , distinct $\beta_1 \rightarrow \beta'_1$ and $\beta'_1 \rightarrow \alpha'_1$ transformations successively took place on loading, and distinct $\alpha'_1 \rightarrow \beta'_1$ and $\beta'_1 \rightarrow \beta_1$ reverse transformations did on unloading.

(2) In the temperature range above T_c , the transformation behavior on loading was the same as that in the temperature range between A_f and T_c . However, on unloading, first the $\beta'_1 \rightarrow \beta_1$ and then continuous $\alpha'_1 \rightarrow \beta'_1 \rightarrow \beta_1$ transformation took place when the loading was stopped on the halfway of the second stage.

(3) Accordingly, the previous interpretation for the unloading process of the s-s curves obtained above T_c was corrected as shown in Fig. 6.

(4) When the loading was performed until the $\beta'_1 \rightarrow \alpha'_1$ transformation on the second stage was completed, the s-s curve showed a clear one stage of the continuous $\alpha'_1 \rightarrow \beta'_1 \rightarrow \beta_1$ transformations on unloading.

(5) The critical stress vs temperature relation was replotted as shown in Fig. 9. The $\alpha'_1 \rightarrow \beta'_1$ reverse transformation stress showed a linear relationship with temperature.

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