Positron Dopplerbroadening Measurements in Cu-Al-Ni Based Shape Memory Alloys

D. Segers, I. Hurtado, L. Dorikens-Vanpraet, J. van Humbeeck

► To cite this version:

D. Segers, I. Hurtado, L. Dorikens-Vanpraet, J. van Humbeeck. Positron Dopplerbroadening Measurements in Cu-Al-Ni Based Shape Memory Alloys. Journal de Physique IV Proceedings, 1995, 05 (C1), pp.C1-163-C1-169. 10.1051/jp4:1995119 . jpa-00253555

HAL Id: jpa-00253555

<https://hal.science/jpa-00253555>

Submitted on 1 Jan 1995

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Positron Dopplerbroadening Measurements in Cu-Al-Ni Based Shape Memory Alloys

D. Segers, I. Hurtado*, L. Dorikens-Vanpraet and J. van Humbeeck*

RUG, Vakgroep subatomaire en stralingsfysica, Proeftuinstraat 86, B-900 Gent, Belgium

** KUL, Departement metaalkunde en toegepaste materiaalkunde, de Croylaan 2, B-3030 Heverlee, Belgium*

Abstract: Positron annihilation Dopplerbroadening measurements were carried out on Cu-Al-Ni based alloys to which Ti, and Ti and Mn was added. The measurements reveal a drastic effect in the S-parameter behavior when the defects anneal out at the transition from martensite to the beta phase. When crossing the transition region several times, an increase of the S-parameter value is observed. This is interpreted as due to the formation of dislocations and precipitate-martensite interfaces. In the alloy with Mn a distinct behavior is observed attributed to vacancy cluster formation.

1. INTRODUCTION

In the industrial application of metals a lot of physical qualities such as tensile strength, ductility, malleability and conductivity, are important. There exists an important class of alloys which exhibit another remarkable quality of memory and trainability. These alloys are called shape-memory alloys. If such alloys are plastically deformed at one temperature, they will completely recover their original shape on being raised to a higher temperature. In recovering to their original shape these alloys can produce a displacement or a force, or a combination of both, as a function of temperature. Because of these remarkable properties, shape-memory alloys can be used in a variety of industrial and medical applications.

All the shape-memory alloys exhibit a transformation from a so called martensite phase to a higher-temperature configuration called the parent or beta phase. The martensite crystal structure is usually produced by rapidly quenching a suitable alloy to some critical temperature. The transformation from the low temperature martensite structure to the higher-temperature meta-stable beta phase is diffusionless, resulting from the coordinated movement of large blocks of atoms. The transformation is also crystallographically reversible.

Martensitic transformations occur in ferrous as well as in non-ferrous martensitic alloys. A lot of Cu-based alloys (such as Cu-Zn, Cu-Zn-Al, Cu-Zn-Ga, Cu-Zn-Sn, Cu-Zn-Si, Cu-Al-Ni, Cu-Sn) have been studied and reveal the shape-memory effect.

The alloys studied in this work are Cu-Al-Ni based. At high temperatures (around 1173K) these alloys are in a stable bcc disordered beta phase. When slowly cooling the alloys, this phase will decompose into other phases which minimize the free energy of the system. However, when quenching the alloy to low temperatures, this phase decomposition is suppressed and the beta phase is frozen-in

When slowly cooling the alloy after the initial water quench from high temperatures, the beta structure transforms to martensite. The volume of the crystal which transforms to martensite will increase with decreasing temperature until the whole crystal has become martensite. By heating the alloy the reverse transformation occurs and a hysteresis effect of 10 to 20 K is seen. The transformation is characterized by four transformation temperatures M_s , M_f , A_s , A_f . M_s and M_f are those temperature where the martensitic transformation starts and finishes (when cooling the alloy from the parent phase). A_s and A_f are those temperature where upon heating the martensitic alloy respectively starts to transform to the beta phase and where the transformation is complete.

Martensitic alloys exhibit a stabilization process. This means that the A_s and A_f temperatures shift to higher values as a function of ageing in the martensite phase. This effect is often detrimental to the industrial application of shape-memory alloys. It is known that the stabilization effect occurs much faster if the vacancy concentration retained in the martensitic phase is higher. To minimize this effect step-quenching is often used. In this process the alloys are first quenched to temperatures just above M_s and then quickly cooled down below M_f .

Positron annihilation is an excellent tool to study vacancy type defects. In the present work this technique is used to study the behavior of quenched in vacancies in a number of Cu-Al-Ni based alloys.

2. EXPERIMENTAL

The samples used had a rectangular shape with dimensions of $10 \times 10 \times 1$ mm³. The base material of the alloys used was Cu-Al-Ni to which Ti, and Ti and Mn was added. The composition of the different alloys and the first re-transition temperatures are given in table 1.

Table 1: Composition of the different alloys and the transition temperatures

ABBREVIATION	COMPOSITION (wt %)	FIRST RE-TRANSFORMATION TEMPERATURES (K)	
		A_s	A_f
CAN	83 Cu - 13 Al - 4 Ni	396	428
CANTI	82.65 Cu - 13.36 Al - 2.99 Ni - 1 Ti	469	505
CANTIM	80.1 Cu - 11.9 Al - 5.0 Ni - 1 Ti - 2 Mn	378	429

All the samples were betatized in air at $T_Q = 1173$ K for $t_Q = 15$ minutes and then quenched into a water bath at $T_B = 273$ K, which is well below the martensite transformation temperatures. Before the measurements the samples were etched in a solution of 50% HNO_3 and 50% water.

As a positron source ^{22}Na was used which was sandwiched between two identical samples. This sandwich arrangement was placed into a vacuum cryostat.

The Dopplerbroadening of the 511 keV positron annihilation line was measured with an intrinsic Ge detector having a resolution of about 1.2 keV at an energy of 511 keV and at a count rate of 8×10^3 counts per second. With a biased amplifier all the pulses below about 380 keV were cut off. Stabilization of the energy spectrum was performed with the help of two ultra-stable pulsers^[1]. The energy calibration of the system was 0.05 keV per channel. The annihilation line was characterized by the conventional S-parameter which is the fraction of full energy counts falling within a central integration window.

The S-parameter was measured in situ as a function of the temperature starting from 100 K up to 600 K in steps of 10 K. Each measurement lasted 15 minutes. Thereafter the temperature was lowered in the same way and several consecutive temperature cycles were measured.

3. RESULTS AND DISCUSSION

3.1 CAN - alloy

The S-parameter measurements for the CAN alloy are represented in figure 1. Only the first heating and cooling run are shown. During the heating run the S-parameter value shows a quite flat plateau in the temperature region from 100K up to 370K. From 370K on a drastic decrease in the S-parameter value is measured up to 430K. Thereafter a rather flat behavior is seen in the temperature region up to 490K and then the S-parameter value starts to increase. In the cooling run the data start deviating significantly from the data of the heating run for temperatures below about 530K. A dip in the data of the cooling run is seen at around 480K. The slope of the data in the cooling run in the temperature interval 100K to 370K is different from the slope of the data in the heating run in the same temperature interval. At 100K a big difference between the data before and after the cycling is seen. This means that by quenching the alloy from $T_Q = 1173\text{K}$ into ice water, vacancies are frozen in. These vacancies disappear at the martensite to beta transformation. In the as-quenched alloys saturation trapping in defects occurs which is characterized by the flat plateau in the temperature region 100K to 370K. After the annealing of the vacancies (i.e. in the cooling down run) the slope in the data in the same temperature interval from 100K to 370K represents the effect of thermal expansion in the martensite phase.

The same alloy was heat treated completely differently. Instead of quenching the alloy, the samples were slowly cooled from high temperatures, so that the beta phase decomposed into other stable phases and consequently the martensite phase did not occur. S-parameter measurements in these samples in the same temperature region are shown in figure 2. The measured S-parameter behavior is completely different. The S-parameter changes very slowly as a function of the temperature and no drastic annealing effect is seen. From the positron annihilation data it is clear that the martensite transformation does not occur.

Figure 1: Positron S-parameter measurements in the base CAN alloy as a function of temperature.

Measurements were also carried out during further cycling the CAN alloy in the interval between 100K and 600K. It was noticed that after the first heating run the curves in the interval 100K-600K always shift to higher S-parameter values with the number of cycles.

Figure 2: S-parameter measurements in the CAN alloy samples which were slowly cooled from 1173K to room temperature so that the martensite phase does not occur

3.2 CANTI alloy

Dopplerbroadening measurements in the CANTI alloy are represented in figure 3. The first heating run from 100K up to 390K shows some temperature dependence. The first heating run was performed up to 390K, then the temperature was lowered again to 100K, and a second heating cycle, up to 600K was started. It is seen that the data for this second heating run is shifted to a lower S-parameter value. The slope of the data for the first heating run is the same as for the second heating run in the as-quenched samples. This indicates that some vacancies may have disappeared by the first heating run up to 390K.

From 380K up to 470K a drastic decrease in the S-parameter values is seen. This indicates again that at the martensite transition the quenched-in vacancies disappear. The data for the first cooling run in the temperature interval 390K-100K show a somewhat steeper slope than the data of the as-quenched sample in the first heating run. The total decrease in S-parameter due to the annealing out of the vacancies is lower in the CANTI sample in comparison with the CAN sample. This could indicate that the quenched-in vacancy concentration in this alloy is lower. The slight temperature slope in the as quenched alloy during the first heating run in the temperature interval 100K-390K could also be explained as non-saturation trapping in the quenched-in defects.

In figure 3 it is also seen that when cycling through the martensite transformation the S-parameter value gradually increases. It is known that when cycling through the martensite transformation, dislocation are formed^[2]. Positron trapping in those generated dislocations occurs so that an increase in the S-parameter is expected. This has been seen with positron annihilation measurements in a ternary Cu-Zn-Al alloy^[3]. However in the former measurements^[3] a significant increase of the S-parameter was seen only after 10 cycles. The effect saturated after about 100 cycles. In the beta phase of that ternary Cu-Zn-Al alloy an increase of the S-parameter value was also seen.

In the CANTI alloy the number of cycles is rather small so that the increase in S-parameter value due to dislocation formation is expected to be small too. It is also seen that in the beta phase the curves practically coincide. This means that dislocation formation alone cannot account for the observed effect. Because the

measurements are performed up to 600K (well above the A_f temperature) and because each measurement lasted 15 minutes, the alloy is kept for an appreciable time in the beta phase. During that time precipitation of other phases (bainite α or γ) can take place. This means that in the martensite phase interfaces of precipitates and martensite plates exist. Besides trapping in dislocations a supplementary positron localization can occur at those interfaces leading to an increase of the S-parameter value.

Figure 3: S-parameter measurements in the CANTI alloy as a function of temperature

3.3 CANTM alloy

The Dopplerbroadening measurements in the CANTM alloy are represented in figure 4. The most remarkable observation in these measurements is that for the as-quenched alloys there is a pronounced temperature dependence in the temperature region 100K-350K. A drastic decrease in the S-parameter value is measured in the interval 370K-470K. In the parent phase an increase of the S-parameter values is obtained. After the annealing-out of the quenched-in defects the curves in the temperature interval 100K-350K display a temperature behavior which is completely different from the one measured in the same temperature interval for the as-quenched alloy. The low-temperature dependence in the as-quenched alloy is hardly understandable with the assumption that mono-vacancies are quenched-in. If the quenched-in vacancy concentration is high enough so that saturation trapping should occur, then practically no temperature dependence (as in the CAN alloy) is expected. If the vacancy concentration is not high enough to result in saturation trapping then some temperature dependence is expected due to the thermal expansion of the lattice. This should resemble the temperature dependence of the data in the low temperature region after the annealing of the quenched-in defects.

In the as-quenched alloy a very steep increase in the S-parameter value is seen for temperatures up to 250K. A very similar behavior (in lifetime measurements) was seen in literature for samples containing large vacancy clusters (voids)^[4]. This temperature effect was explained as being due to the temperature dependence of the positron trapping probability which at low temperatures is transition limited and strongly dependent on the temperature and which at higher temperatures is diffusion-limited and weakly temperature dependent. These results suggest that the addition of Mn favors the nucleation of large

vacancy clusters. Such Mn-vacancy associations in a CANTIM alloy have already been proposed by Dunne et al.^[5] based on anomalous DSC measurements. Nevertheless, such anomalous behavior has not been observed for a Cu-Al-Ni-Mn alloy^[6]. Thus further experiments are needed to determine if the presence of Ti is a necessary condition for the observed S-parameter behavior.

Figure 4: S-parameter data in the CANTIM alloy samples

The reversibility of the data in the low temperature region for the as-quenched samples was checked by cycling in the temperature interval between 100K and 310K. The data always coincide. The measurements are represented in figure 5. Those measurements were performed on samples which were aged for about 4 month in the martensite phase at room temperature. After having measured four cycles in the low temperature interval the samples were measured crossing the martensite transformation region. A drastic decrease in the S-parameter value is seen.

4. CONCLUSION

From the data presented in this work it is clear that positron annihilation is a very useful tool to study industrial materials. The measuring technique is very sensitive to the presence of defects and can be used to follow the defect behavior in industrial alloys. However in comparison with simple metals (or even simple binary alloys) the interpretation of the data in real industrial materials is not always straight forward. Impurities are added to the basic alloys to improve the metallurgical properties, but introduce a lot of physical complications on the atomic scale (defect-impurity interaction, impurity-impurity interactions, ...). The positron annihilation technique provides a lot of useful information which can be used to interpret metallurgical problems when combining the data with data obtained from other techniques. This implies a close collaboration between the positron physicist and the metallurgists.

Figure 5: S-parameter measurements in an aged CANTIM alloy in order to check the reversibility in the low temperature region of the as-quenched alloy

ACKNOWLEDGMENTS

This work was part of the IIKW program 4.0006.92 and the FKFO program 2.0093.93. Financial support is acknowledged.

REFERENCES

- [1] Dorikens M., Van den Bossche K., Dorikens-Vanpraet L., Segers D. and Lemahieu I., "Proceeding of the 7th international conference on positron annihilation", New Delhi, India 1985, Ed. P.C. Jain, R.M. Singru and K.P. Gopinathan (World Scientific), pp. 819-821
- [2] Rios Jara D., Morin M., Esnouf C. and Guénin G., J. Physique 43, (1982) C4-735
- [3] Segers D., Van Humbeeck J., Delaey L., Dorikens M. and Dorikens-Vanpraet L., Appl. Phys. A36, (1985) 179-182
- [4] Nieminen R.M., Laakkonen J., Hautojärvi P. and Vahanen A., Phys. Rev. B (1979) 1397-1402
- [5] Dunne D.P., Van Humbeeck J. and Delaey L., "Proceedings of MRS conference on Advanced materials", Tokyo, (1988) 9, 329
- [6] Heycott A.J., Dunne D.P. and Kennon N.F., Mater. Sci. Forum 56-58 (1990) 475