Journal of Thermal Analysis, Vol. 17 (1979) 489–494

A THERMAL X-RAY AND RESISTIVITY STUDY OF THE HEUSLER ALLOY Cu_2NiSn*

W. H. SCHREINER, P. PUREUR, T. A. GRANDI, J. V. KUNZLER and D. E. BRANDÃO

Instituto de Fisica, UFRGS, Porto Alegre, Brasil

(Received January 16, 1979)

The compound Cu_2NiSn was analyzed by DTA, X-ray and electrical resistivity measurements. No single-phase structure was found at room temperature. The alloy decomposes upon heating, starting at 160°, forming copper and two hcp structures. At 500° the Heusler structure is restored. Electrical resistivity results are discussed in terms of Markowitz's theory for disordered metals.

The Heusler alloys are intermetallic compounds with stoichiometric composition X_2YZ and the crystallographic $L2_1$ structure. X, Y and Z may be chosen to cover several elements, but the vast majority of the studied alloys contains Mn as the Y element. X is generally one of the noble metals, while Z is commonly one of the *s-p* elements. The alloys containing Mn are strongly ferro- or antiferromagnetic with $\sim 4\ \mu_B$ localized on the Mn site [1].

The alloy Cu_2NiSn is known to be diamagnetic [2], showing that the Ni atoms carry no magnetic moment in this compound, and further, it is said to be of single phase [2–4] with a lattice parameter $a_0 = 5.96_6$ Å [2].

According to Dokuzoguz [3] the Mössbauer spectrum shows an unusual splitting, since the alloy is considered to be of cubic symmetry. This splitting is said to be explained on the assumption of a disordered $NiCu_2$ sublattice, so that Cu_2NiSn would not really be of Heusler, but of the DO_3 (Fe_3Al type) structure.

The exceptionally high residual resistivity of $\sim 49\ \mu\Omega$.cm attributed to this alloy [2] is also rather unusual for an ordered metallic structure.

These two unusual properties, together with its diamagnetic behaviour, make this alloy interesting for further study.

Experimental

The purity of the starting metals was 3 N for Cu and Sn and 4 N for Ni. The constituents were melted at 1100° in evacuated quartz ampoules and heat-treated for 2 days at 700°. The resistivity samples were cut by spark-erosion ($1 \times 1.5 \times 15$ mm)

* Work supported in part by Conselho Nacional de Desenvolvimento Cientifico e Tecnologico (CNPq) and Financiadora de Estudos e Projetos (FINEP).

and part of the alloy was powdered to 270 mesh size for DTA and X-ray analysis. Samples and powder were further annealed at 700° in evacuated quartz ampoules for 1 day and quenched in cold water.

The thermoanalysis measurements were obtained on a Paulik–Paulik–Erdey type derivatograph (MOM), with heating at 6°/min in an Ar atmosphere.

A Rigaku X-ray diffractometer was used for the structural analysis. The resistivity measurements were performed from room temperature up to 700° in a vacuum chamber by the standard four-point DC technique. A Keithley 180 nanovoltmeter and a Keithley 227 current source were employed. The temperature control unit was driven by a chromel-alumel thermocouple. The heating and cooling rates were approximately 1.2°/min and 3.4°/min, respectively.

Results

The DTA result is shown in Fig. 1. This measurement clearly shows exothermic behaviour for Cu_2NiSn up to 400°, followed by a sharp endothermic movement until 495° is reached. Another thermal movement appears at 620°. No mass variations occurred, as ascertained in a simultaneous thermogravimetry measurement, and therefore this alloy shows structural phase transitions.

The X-ray analysis was based in part on the DTA results. The powder quenched from 700° exhibited the expected Heusler cubic superstructure lines. The lattice parameter calculated using the Nilson–Riley technique [5] was in good agreement with Endo's and Dokuzoguz's results [2, 3], as shown in Table 1. The visual colour of the alloy appeared metallic gray. A small non-cubic phase precipitation was also present, but its structure could not be determined due to the faintness and scarcity of the diffraction lines. It was found that the quenching time had no influence on this additional precipitation, and even normal cooling from 700° was ineffective. The powder was then annealed at the following temperatures, each for 1 day, followed by quenching and sometimes by slow cooling: 100, 245, 335, 400, 500 and

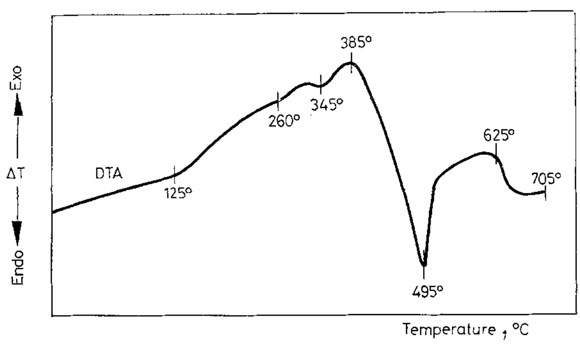

Fig. 1. Differential thermal analysis of Cu_2NiSn

Table 1

Lattice parameters of the observed structural phases in Cu_2NiSn

Structure	a, Å	c/a	Quenching temp. range, °C
$L2_1$	5.964 ± 0.007	1	500–700
hcp (1)	4.12	1.26	245–400
hcp (2)	4.14	1.24	
fcc	3.63	1	
Copper*	3.615	1	

* Reference [10]

580°. These were selected on the basis of the inflection points in the DTA curve. New diffraction lines started to appear for the powder treated at 245°. These lines are also present for the annealings at 335 and 400°. Three new structural phases could be determined: two hcp and one fcc. The lattice parameters and c/a values are also listed in Table 1. The colour of the powder appeared golden. A return to the Heusler structure was noted for the annealing at 500° and the small non-cubic phase precipitation appeared again, while the cooling rate from 500° did not alter the diffraction pattern.

The electrical resistivity $\rho(T)$ curve for Cu_2NiSn is shown in Fig. 2. Three samples were measured, with similar results. The error in the absolute value for ρ is approximately 2%, mainly due to the geometrical factor. The very high $\rho(20°)$ was expected in view of Endo's [2] results. A linear variation with T was observed for the resistivity from 20 to 160°. After this, a saturation and a fall are noted and a minimum is reached near 410°, followed by a sharp increase until 500° where new linear be-

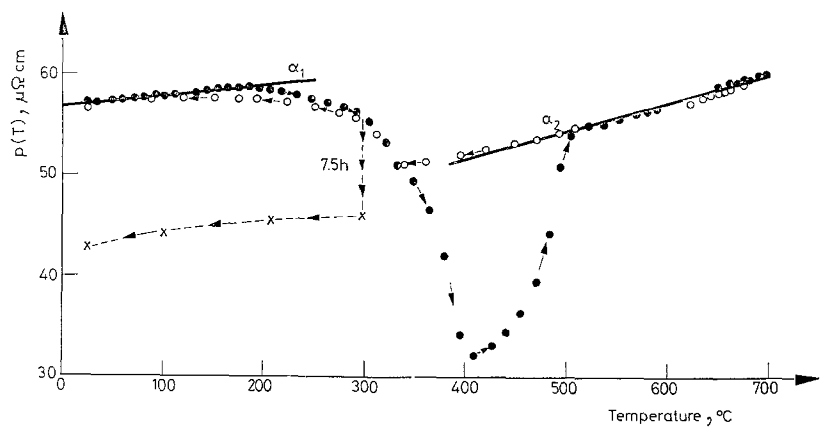

Fig. 2. Electrical resistivity curves for Cu_2NiSn. The crosses represent experimental points after a 7.5 h annealing at 300° followed by cooling. ● Heating; ○ cooling

haviour up to 700° is observed. In the cooling return curve this linearity extends down to 330° and the minimum does not occur. From 330° to room temperature the cooling and heating curves are not very different. This similarity is evidence of partial reversibility. However, in another experiment, where the temperature was held at 300° for 7.5 h, a marked reduction of the resistivity was revealed, as shown in Fig. 2.

The two temperature coefficients of resistivity, α, for the linear parts of the $\rho(T)$ curve were calculated by a least square fit, to give:

$$\alpha_1 = 1.85 \times 10^{-4}\,{}^\circ C^{-1} \qquad 20^\circ < T < 160^\circ \qquad r^2 = 0.998$$

$$\alpha_2 = 6.6 \times 10^{-4}\,{}^\circ C^{-1} \qquad 330^\circ < T < 700^\circ \qquad r^2 = 0.990$$

where r^2 is the squared linear correlation coefficient of the fit. The fit is only reasonable for the higher temperature range, caused perhaps by a small quadratic term from thermal expansion of the lattice [6].

Discussion

The alloy shows a clear cubic Heusler structure, together with a small non-cubic precipitation, in the X-ray diffraction pattern when quenched or slow-cooled from temperatures higher than 500°. The exo- and endothermic movements in the DTA result support this finding. The thermal movement at 620° is not detected in either X-ray or resistivity measurements.

Upon heating to 400° Cu_2NiSn suffers an exothermic structural change. The golden aspect, the reduction of the resistivity and the new cubic phase in the diffraction pattern suggest a cluster formation of Cu atoms. Concomitantly, two hexagonal close-packed structures appear, resembling those presented by $Ni_3Cu_2Sn_3$ and Ni_6CuSn_5, studied by Mazzoleni [7]. The sharp endothermic part from 400 to 500° in the DTA curve corresponds to a clear increase in resistivity behaviour. The Heusler phase is restored. The lower resistivity at 500° as compared to room temperature evidences a more ordered alloy at this higher temperature. This is in agreement with the difference in the temperature coefficients of the linear parts of the resistivity curve and could be understood in terms of Markowitz's [8] theory for very resistive metals, where the mixing of disorder and phonon scattering leads to an ideal resistivity which is proportional to the residual resistivity and to the Debye-Waller factor $e^{-2W(T)}$. According to Markowitz, in the high-temperature limit:

$$\begin{aligned}\rho(T) &\cong \rho_0 + (\eta - 2\,W_1\rho_0)\frac{T}{\theta_D} \quad (T > \theta_D)\\ &= \rho_0 + \alpha\rho(0^\circ)T\end{aligned}$$

where ρ_0 is the residual resistivity and η is the usual electron-phonon resistivity coefficient, written as

$$\rho_i = \eta\,\frac{T}{\theta_D},$$

θ_D is the Debye temperature and for W the asymptotic high-temperature expression $W = W_1T/\theta_D$ [9] is taken, where W_1 is independent of the temperature. Then, the temperature coefficient of resisitivity is given by

$$\alpha = \frac{1}{\rho(0°)} \frac{(\eta - 2\,W_1\rho_0)}{\theta_D}.$$

The difference in the two α's is due to a change in ρ_0. In the range $20° < T < 160°$ the lower α_1 corresponds to a higher ρ_0, which is also reported by Endo et al. [2]. This indicates a somewhat disordered structure, or a mixture of structures, as detected in the X-ray diffraction pattern, and could also explain Dokuzoguz's [3] results, where an unusual splitting is observed in the Mössbauer spectrum. In the temperature range from 700 to 330°, where a higher α_2 was found, a lower ρ_0 is expected. This leads to the speculative assumption that Cu_2NiSn is in the Heusler single phase above 500°, with the absence of other structural phases. The anomalous behaviour of the resistivity in the range $160° < T < 330°$ is in part reversible if the experiment is conducted rapidly. Upon cooling, an order-disorder process is clearly noted. On the other hand, an irreversible component has to be present also, since long experimental times reduce the resistivity markedly at a temperature just below 330°. Between 330 and 410° this irreversible component dominates, even with short experimental times, and the formation of copper clusters tend to short-circuit the electrical path through the specimen. The somewhat higher a_0 value for these clusters as compared to the literature value [10] for pure copper is acceptable, since these clusters are not of high purity and are in a different structural environment.

Upon cooling from 700°, clustering is not present and the Heusler structure does not deteriorate between 500 and 330°. This behaviour presumably led the various authors [2, 3] to the conclusion that this alloy has a Heusler single-phase structure.

It is remarkable that the strong temperature dependence of the resistivity observed for the ferromagnetic alloy Cu_2MnAl [11] is absent in this diamagnetic alloy, where it is structurally stable.

Conclusion

Cooling the alloy Cu_2NiSn from above 500° leads to a Heusler structure, together with a small non-cubic precipitation. However, upon heating, the Heusler structure decomposes gradually, starting at 160°, but forms again at 500°. In limited structurally stable regions the resistivity behaviour gives evidence of the correctness of the Markowitz theory for disordered metals, while the strong temperature dependence observed for the Heusler alloy Cu_2MnAl is absent. It is clear that very valuable information for thermal analysis is provided by electrical resistivity measurements.

References

1. P. J. Webster, Contemp. Phys., 10 (1969) 559.
2. K. Endo, K. Tabushi and R. Kimura, J. Phys. Soc. Japan, 32 (1972) 285.
3. H. Z. Dokuzoguz, H. H. Stadelmaier and L. H. Bowen, J. Less-Common Metals, 23 (1971) 245.
4. R. N. Kuz'min, N. S. Ibraimov and G. S. Zhdanov, Sov. Phys. JETP, 23 (1966) 219.
5. A. Taylor and H. Sinclair, Proc. Phys. Soc., 57 (1945) 126.
6. N. F. Mott and H. Jones, The Theory of Properties of Metals and Alloys, Dover 1955, p. 268.
7. F. Mazzoleni, Metallurgia Italiana, 45 (1953) 366.
8. D. Markowitz, Phys. Rev. B, 15 (1977) 3617.
9. J. M. Ziman, Principles of the Theory of Solids, Cambridge, 1972, p. 64.
10. R. W. G. Wykoff, Crystal Structures, 2nd., Interscience, 1965, p. 10.
11. J. V. Kunzler, T. A. Grandi, W. H. Schreiner, P. Pureur and D. E. Brandão, J. Phys. Chem. Solids, 40 (1979) 427.

Résumé — Le composé Cu_2NiSn a été examiné par ATD, rayons X et mesures de résistance électrique. A température ambiante on n'a pas trouvé de structure correspondant à une phase unique. L'alliage se décompose par chauffage à partir de 160° en formant du cuivre et deux structures hcp. A 500° la structure Heusler est rétablie. On discute les résultats des mesures de résistance électrique à partir de la théorie de Markowitz pour des métaux désordonnés.

Zusammenfassung — Die Verbindung Cu_2NiSn wurde durch DTA, Röntgen- und elektrische Widerstandsmessungen analysiert. Keine Einphasenstruktur wurde bei Zimmertemperatur gefunden. Die Legierung zersetzt sich beim Erhitzen ab 160°, wobei Kupfer und zwei hcp-Strukturen gebildet werden. Bei 500° wird die Heusler-Struktur wieder hergestellt. Die Ergebnisse der elektrischen Widerstandsmessungen werden aufgrund der Markowitzschen Theorie für ungeordnete Metalle diskutiert.

Резюме — Соединение Cu_2NiSn было исследовано с помощью ДТА, рентгеновской диффракции и измерениями электрического удельного сопротивления. При комнатной температуре не было найдено однофазной структуры. Этот сплав при нагревании разлагается, начиная при 160° и образуя при этом медь и две гексагональные структуры с плотной упаковкой. При 500° восстанавливается структура Хеслера. Результаты электрического удельного сопротивления обсуждены на основе теории Марковица для нарушенных металлов.