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THERMAL AND MAGNETIZATION STUDIES ON HEUSLER ALLOYS*

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Saturation magnetization measurements as a function of temperature were performed on $Cu_2Mn(Al_{1-x}Sn_x)$ Heusler alloys to study the existence of stable structures. The derivatograph was applied to study the thermal effects.

The Heusler alloys are a group of ternary intermetallic compounds formed with stoichiometric composition X_2YZ, and with the doubly-ordered $L2_1$ type structure shown in Fig. 1 [1]. The structure is cubic with the X atoms at the cube corners and Z and Y atoms at alternate body centers. Generally, X is a transition metal, Y is normally Mn, and Z is a transition metal such as Al, Sn, Sb, etc.

Another crystallographic structure that may occur at the stoichiometric composition X_2YZ particularly for Cu_2MnAl is the $B2$ structure, characterized by Y–Z disorder. The occurrence of the $L2_1$ or $B2$ phase is a function of the heat treatment of the material, and the range of temperature in which each phase exists depends on the alloy studied. There may occur, too, the precipitation of other phases, not at the stoichiometric composition X_2YZ, for well-defined temperature ranges, depending on the alloy [2].

The Heusler alloys have been of interest since 1903, when Heusler [3] reported that ferromagnetic alloys could be made from the non-ferromagnetic constituents copper–manganese and group B elements such as aluminium and tin. Since then, a great number of ternary alloys with ferromagnetic or antiferromagnetic properties have been detected and classified in terms of the most abundant element, giving rise to the so-called Heusler alloy series. Most of the experimental work on Heusler alloys is concerned with their crystallographic structures. It is well established that they are very sensitive to heat treatment and composition, and this fact probably explains the incomplete agreement between the data available in the literature relating to temperatures and crystallographic phases [4].

One of the most studied Heusler alloy families is the copper series and mainly the alloys Cu_2MnAl and Cu_2MnSn. The present work studies the temperature behaviours of the Heusler alloys of the $Cu_2Mn(Al_{1-x}Sn_x)$ type, by a derivato-

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graph and by saturation magnetization measurements. The purpose of this study is to detect the existence of stable structures, obtained from Cu_2MnAl by substitutional addition of tin atoms, with reversible saturation magnetization behaviour. Knowledge of the stable structures so obtained will be of interest for the theories being developed to describe Heusler alloys.

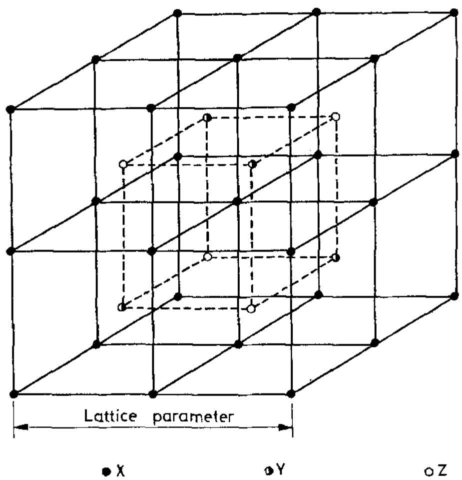

Fig. 1. Heusler alloys structure

Sample preparations

The samples were prepared by heating the constituents, mixed in stoichiometric quantities, in an electrical furnace in vacuum. The final mass of each sample was about 15 g and the loss during the melting process was smaller than 0.4%. Each of the elements used in the preparation of the alloys was at least 99.9% pure. All samples were heated in alumina crucibles, annealed at 750° for one day, and quenched in cold water at a rate of 150°/min. They were then pulverized for thermal and magnetization measurements.

X-ray diffraction measurements were performed in order to determine the lattice parameters of the alloys. Very good agreement was found with the published data on Cu_2MnAl [5]. Table 1 shows the results obtained. It is interesting to note that as the tin concentration increases, there appear two lattice parameters, indicating the coexistence of Cu_2MnAl with Sn and Cu_2MnSn with Al structures. In the case of $Cu_2Mn(Al_{0.25}Sn_{0.75})$ the lattice parameter value is quite similar to the known value for Cu_2MnSn [5].

Experimental procedures

Thermal analyses were carried out using a Paulik–Paulik–Erdey-type "Derivatograph" model 1969, manufactured by MOM, Budapest. Measurements were performed, in an argon atmosphere at a heating rate of 10°/min, using 1 g of powdered material.

Measurements of the saturation magnetization as a function of the temperature were carried out using a vibrating sample magnetometer, based on the design of Foner [6], and modified by Cochrane [7]. The magnetometer was charged with 15 mg of powdered material, heated at a rate of 2°/min, at a pressure of 10^{-2} torr.

Table 1

Lattice parameters from X-ray analysis

Alloy	Lattice parameter, Å
Cu_2MnAl	5.96
$Cu_2MnAl_{0.9}Sn_{0.1}$	5.99
$Cu_2MnAl_{0.75}Sn_{0.25}$	5.98 and 6.12
$Cu_2MnAl_{0.50}Sn_{0.50}$	5.94 and 6.12
$Cu_2MnAl_{0.25}Sn_{0.75}$	6.14

Table 2

Melting points and critical temperatures obtained from DTA and saturation magnetization measurements

Alloy	Melting point, °C	Critical temp., °C
Cu_2MnAl	–	360*
$Cu_2MnAl_{0.9}Sn_{0.1}$	–	372±2
$Cu_2MnAl_{0.75}Sn_{0.25}$	710±5	330*
$Cu_2MnAl_{0.50}Sn_{0.50}$	700±5	–
$Cu_2MnAl_{0.25}Sn_{0.75}$	685±5	–

* Qualitative data due to structural instability.

Discussion

The differential thermal analysis (DTA) curves (see Fig. 2) show, for all the alloys studied, an endothermic reaction at $50° \leq T \leq 120°$, followed by exothermic behaviour at $120° \leq T \leq 250°$. These two DTA regions are connected with structural and spin ordering process, as may be confirmed by the saturation magnetization measurements described below. In the case of the Cu_2MnAl alloy it is known [8] that both the saturation magnetization and the critical temperature change on heat treatment: both show minimum values in the state quenched from high temperatures and increase with aging at low temperatures.

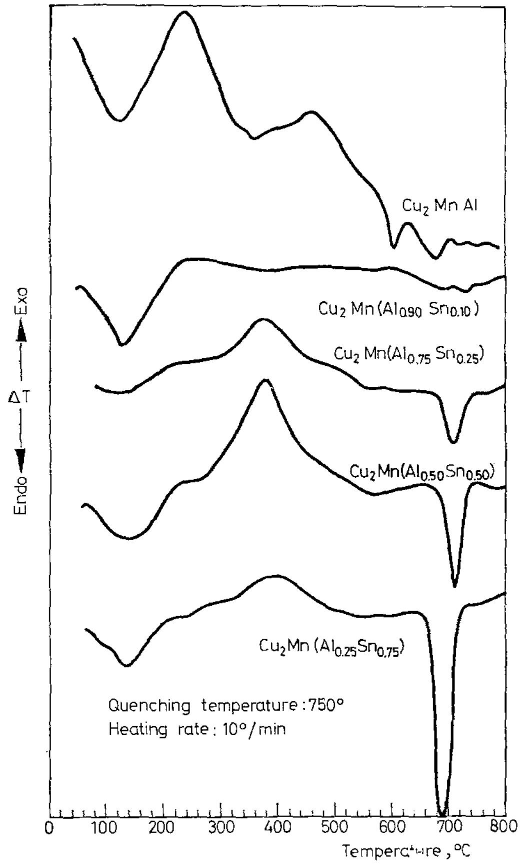

Fig. 2. DTA curves from 50° to 800°

The saturation magnetization measurements shown in Fig. 3 were performed in two steps: a) from room temperature to 240°, where the curves present a maximum; b) after cooling to room temperature, the measurements were performed up to 410°. In the first step (20° ≤ T ≤ 240°) we can distinguish two parts: the first one presents almost flat behaviour of the magnetization up to 120°, corresponding to the endothermic process shown by DTA; the second part corresponds to an increase in the magnetization for 120° ≤ T ≤ 240°, in agreement with the exothermic region in the DTA curve. In the second step of the magnetization measurements ($20° \leq T \leq 410°$) it was found that the only stable structure, with a reversible saturation magnetization curve, was $Cu_2Mn(Al_{0.90}Sn_{0.10})$, in agreement with the very flat behaviour presented in the DTA curve for $360° \leq T \leq$ $\leq 560°$. The magnetization curve of $Cu_2Mn(Al_{0.75}Sn_{0.25})$ for $T > 300°$ show a much faster decrease with temperature than the other two alloys studied. Thi

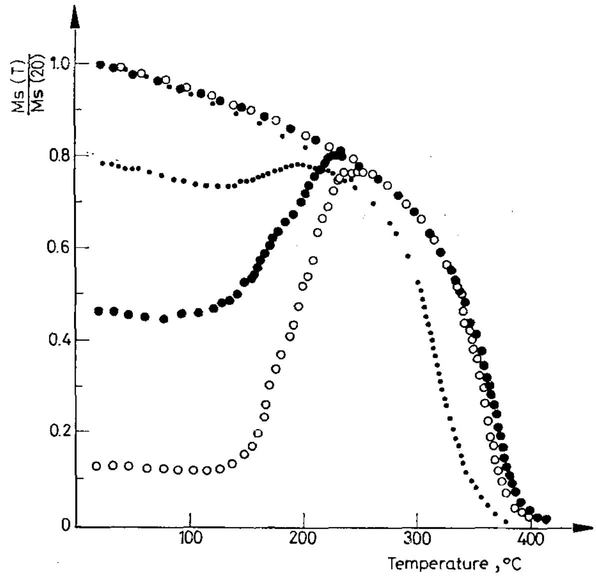

Fig. 3. Saturation magnetization *vs.* temperature from 20° to 410°. o Cu_2MnAl; ● $Cu_2Mn(Al_{.9}Sn_{.1})$; ● (small point) $Cu_2Mn(Al_{.75}Sn_{.25})$; $H = 6$kG; $TT = 750°$

corresponds in the DTA measurement to exothermic behaviour, that extends from 300 up to 380°. The same DTA behaviour is observed in the alloys $Cu_2Mn(Al_{0.50}Sn_{0.50})$ and $Cu_2Mn(Al_{0.25}Sn_{0.75})$. The effect of this phase precipitation on the saturation magnetization measurements is severe, so that no useful curves could be obtained. From the DTA and saturation magnetization curves of Figs 2 and 3 it is possible to obtain the melting points and critical temperatures of some of the alloys studied, as listed in Table 2.

The critical temperature of Cu_2MnAl in the present work is in good agreement with the more recent data available in the literature [9].

The electric resistivity measurement curves of Kimura et al. [10] show inflection points at 350, 500, 550, 630 and 700°. For Cu_2MnAl, some special modifications of the DTA curve occur at these temperatures (Fig. 2).

The present work will be continued by studying the DTA and magnetization behaviours of these Heusler alloys as a function of the heat treatment. This study will be complemented by measurements of the electric resistivity and Mössbauer effect as a function of the temperature ($20° \leq T \leq 650°$).

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Résumé — Etude de l'existence d'une structure stable dans les alliages de Heusler $Cu_2Mn(Al_{1-x}Sn_x)$, à l'aide d'un Derivatograph et par des mesures de magnétisation à saturation en fonction de la température.

Zusammenfassung — Sättigungsmagnetisierungsmessungen als Funktion der Temperatur sowie Derivatographie wurden an Heusler-Legierungen der Formel $Cu_2Mn(Al_{1-x}Sn_x)$ zu Untersuchungen der Existenz einer stabilen Struktur vorgenommen.

Резюме — Для изучения наличия стабильной структуры в сплавах Хеслера$Cu_2Mn(Al_{1-x}Sn_x)$, были использованы измерения магнитного насыщения, как функция температуры, и дериватографический метод. Разработано применение этих комбинированных методов для изучения термической обработки.