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KINETICS OF MARTENSITIC TRANSFORMATION IN CuAlNi-43# ALLOY *

XIONG LIU, TIANHUI SU and LUO PU

Institute of Precious Metals, Kunming (People's Republic of China)

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ABSTRACT

The kinetic process of martensitic transformation occurring in CuAlNi-43# alloy has been investigated using differential scanning calorimetry. From a least-squares fitting of the experimental results using a microcomputer, it is shown that this transformation follows the nucleation-growth law with $n = 1.5$ and that $f(\alpha) = 1.5(1-\alpha)[-\ln(1-\alpha)]^{1/3}$. The activation energy E for this transformation is 53.0 kJ mol^{-1} and the apparent pre-exponential factor A is 1.2×10^{14}.

INTRODUCTION

The alloy CuAlNi-43# is a shape memory material at low temperature. For this group of alloys, which exhibits a thermo-elastic martensitic transition, the process of transformation was mainly studied in the past via microstructural analysis [1]. In recent years, some authors [2–5] have employed resistance measurement, differential thermal analysis (DTA) and differential scanning calorimetry (DSC) to determine the characteristic temperatures of martensitic transformation and its converse process, as well as the effect of thermo-cycles and various heat treatment conditions on the temperatures obtained. In the present paper, results on the martensitic transition kinetics for samples of CuAlNi-43# alloy as established by DSC will be briefly presented. Kinetic parameters have been determined and the mechanism of the transformation has been deduced from the experimental results.

The martensitic transformation is a "congruent" transition process; that is to say, a change in the fraction of transition α can quickly follow a change of temperature, even in the ordinary non-isothermal case. According to

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TABLE 1

The mechanism functions $f(\alpha)$ involved in a solid phase transformation

No.	Symbol	Mechanism	Expression for $f(\alpha)$
1	D_1	1-Dimensional diffusion	$0.5\alpha^{-1}$
2	D_2	2-Dimensional diffusion	$[-\ln(1-\alpha)]^{-1}$
3	D_3	3 – Dimensional diffusion (spherical symmetry)	$1.5(1-\alpha)^{2/3}[1-(1-\alpha)^{1/3}]^{-1}$
4	D_4	3-Dimensional diffusion (cylindrical symmetry)	$1.5[(1-\alpha)^{-1/3}-1]^{-1}$
5	A_1	Nucleation growth ($n=1$)	$(1-\alpha)$
6	$A_{1.5}$	Nucleation growth ($n=1.5$)	$1.5(1-\alpha)[-\ln(1-\alpha)]^{1/3}$
7	A_2	Nucleation growth ($n=2$)	$2(1-\alpha)[-\ln(1-\alpha)]^{1/2}$
8	A_3	Nucleation growth ($n=3$)	$3(1-\alpha)[-\ln(1-\alpha)]^{2/3}$
9	A_4	Nucleation growth ($n=4$)	$4(1-\alpha)[-\ln(1-\alpha)]^{3/4}$
10	R_2	Phase boundary reaction (cylindrical symmetry)	$2(1-\alpha)^{1/2}$
11	R_3	Phase boundary reaction (spherical symmetry)	$3(1-\alpha)^{2/3}$
12	P_1	Power law	1
13	P_2	Power law	$2\alpha^{1/2}$
14	P_3	Power law	$3\alpha^{2/3}$
15	P_4	Power law	$4\alpha^{3/4}$
16	C_1	Chemical reaction (1st order)	$(1-\alpha)$
17	$C_{1.5}$	Chemical reaction (1.5 order)	$(1-\alpha)^{3/2}$
18	C_2	Chemical reaction (2nd order)	$(1-\alpha)^2$
19	Au	Autocatalytic reaction	$\alpha(1-\alpha)$

Sestak's study [6] of non-isothermal kinetics, this transformation may be described by the following expression

$$\frac{d\alpha}{dT}=\frac{A}{\beta}\exp\left(\frac{-E}{RT}\right)f(\alpha) \tag{1}$$

where α is the fraction of transition, T the absolute temperature, A the pre-exponential factor, β the heating (or cooling) rate, E the activation energy of transition, R the gas constant, and $f(\alpha)$ is a characteristic function describing the mechanism of the transformation (see Table 1).

When the investigation is carried out using DSC, α may be obtained from the ratio of the partial area enclosed by the DSC peak at temperature T to the total area under the DSC peak. Because the sample weight employed is so small in this method, the temperature gradient in the sample can be neglected. Therefore the method is well suited to the study of the kinetics of martensitic transformation.

EXPERIMENTAL

The raw material for the CuAlNi-43# alloy with a nominal composition is melted in an aluminium oxide crucible in a vacuum tungsten-wire furnace and then cast into a slab graphite mould. It is then rolled out into a thin sheet at high temperature (about 1000 °C). The specimen used in the experiment is obtained from the sheet after heat treatment at 900 °C followed by quenching in water. The differential scanning calorimetry measurements are carried out using a Thermoflex low temperature DSC device. The scanning temperature range is 80–300 K and the sample weight is about 10 mg. Determinations are carried out at four rates in the range 2.5–20 K min^{-1}. The coolant adopted is liquid nitrogen. In order to avoid any effects of frost on the sample surface during low temperature experiments the sample is kept throughout in an atmosphere of high-purity nitrogen, especially when it is introduced into the DSC cell.

The experimental data are collected and processed by a BX-30 microcomputer after analogue-to-digital transformation at the interface. A program written by ourselves was used to obtain values of various kinetic parameters and to evaluate the transformation mechanism (see Fig. 1). The steps in the procedure are as follows. First, all collected data are successively fitted by a least-squares method for the nineteen mechanism functions listed in Table 1. The correlation coefficients R and standard deviations S of every fitting are calculated. Next, optimum fitting functions $f(\alpha)$ for every group are chosen from the nineteen mechanisms (they are divided into six groups); in this case, the maximum of R/S is regarded as the deciding condition. The corresponding activation energies E and pre-exponential factors A are solved simultaneously. Thirdly, the value of the pre-exponential factor is compared with a predetermined criterion; e.g., it is generally agreed that the value of the apparent pre-exponential factor should be 10^6–10^{20} in common solid-state reactions. Bearing in mind the effect of the experimental precision of the thermal analysis method on the determination of kinetic parameters and the fact that not all the transformation processes studied are decomposition reactions, the range values of A is larger than that reported in refs. 6 and 7.

If a unique function $f(\alpha)$ still cannot be obtained by means of the foregoing selection steps, the "activation energy criterion" may finally be used to achieve the goal. The activation energy can be obtained using Ozawa's (or Kissinger's) method (or by other experiments) and then taken as an initial value E_0 for the activation energy. Based on the condition of least difference between the activation energy concerned and E_0, the most appropriate function $f(\alpha)$ is chosen in each of the remaining selection steps. The overwhelming majority of experiments confirm that this procedure is successful in identifying the most appropriate function $f(\alpha)$ for the process studied.

RESULTS AND CONCLUSIONS

The following experimental results were obtained for the CuAlNi-43# alloy.

When the heating rate is 10 K min^{-1}, the initial temperature at which martensitic transformation commences is 157 K; the final temperature 131 K. The mean activation energy obtained using Ozawa's method is $E_0 = 52.3$ kJ mol^{-1} for the heating rates 2.5, 5, 10 and 20 K min^{-1}. The fittings of the experimental data under each scanning rate with the nineteen mechanism functions, together with the calculated kinetic parameters, are listed in Table 2.

In accordance with the above-mentioned criteria, it is concluded that the mechanism of the martensitic transformations of the CuAlNi-43# alloy at

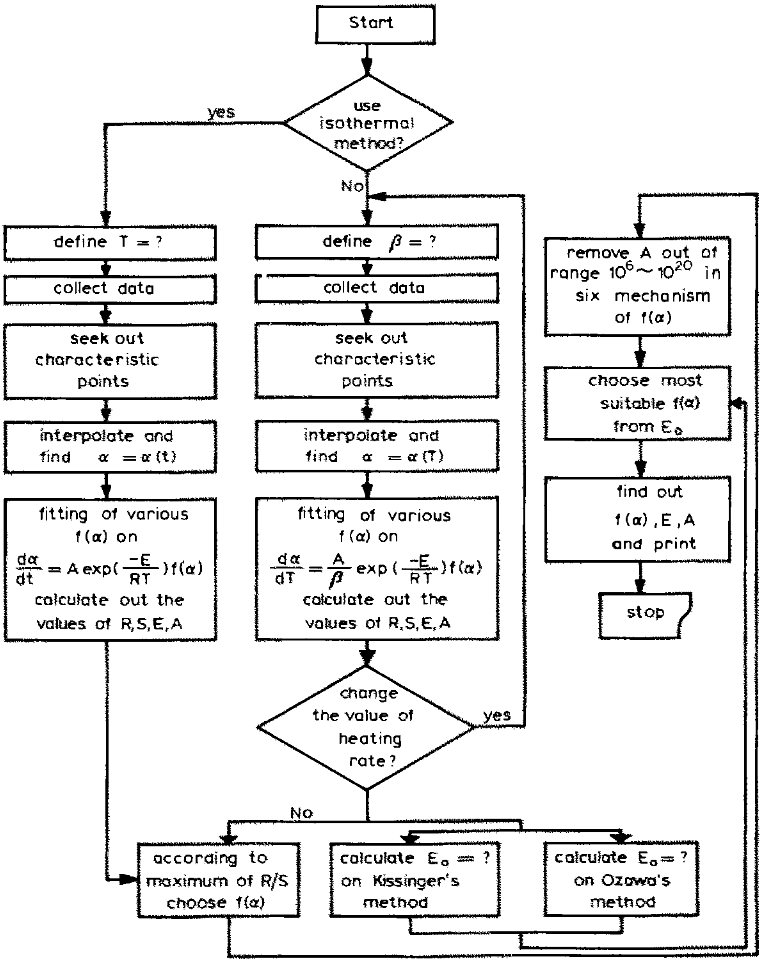

Fig. 1. Block diagram of application programs in the kinetic analysis of solid-state reactions.

TABLE 2

The fitting of various experimental results with each $f(\alpha)$ function

Symbol	Scanning rate							
	2.5 K min^{-1}				5 K min^{-1}			
	E (kJ mol^{-1})	A	R	S	E (kJ mol^{-1})	A	R	S
D_1			0.9812	0.325			0.9877	0.298
D_2			0.9880	0.281			0.9938	0.244
D_3			0.9904	0.268			0.9948	0.216
D_4	390.1	$> 2.57\times10^{75}$	0.9948	0.220	397.8	$> 1.01\times10^{75}$	0.9976	0.157
A_1			0.9889	0.162			0.9876	0.149
$A_{1.5}$	51.7	2.96×10^{13}	0.9966	0.021	52.2	6.42×10^{13}	0.9995	0.008
A_2			0.9967	0.029			0.9996	0.011
A_3			0.9968	0.043			0.9996	0.017
A_4			0.9969	0.131			0.9996	0.051
R_2			0.9915	0.124			0.9957	0.099
R_3	193.0	3.38×10^{67}	0.9939	0.110	197.2	2.34×10^{67}	0.9975	0.078
P_1			0.9889	0.162			0.9876	0.149
P_2			0.9803	0.081			0.9872	0.074
P_3			0.9797	0.054			0.9860	0.049
P_4	38.1	2.93×10^{8}	0.9791	0.040	39.1	9.94×10^{8}	0.9863	0.037
C_1	214.5	$> 2.57\times10^{75}$	0.9968	0.087	217.8	$> 1.01\times10^{75}$	0.9996	0.034
$C_{1.5}$			0.9890	0.214			0.9915	0.221
C_2			0.9960	0.114			0.9908	0.091
Au	57.5	7.65×10^{-22}	0.2044	0.997	52.6	5.05×10^{-19}	0.3127	0.914

Symbol	Scanning rate							
	10 K min^{-1}				20 K min^{-1}			
	E (kJ mol^{-1})	A	R	S	E (kJ mol^{-1})	A	R	S
D_1			0.9808	0.323			0.9823	0.329
D_2			0.9872	0.282			0.9890	0.283
D_3			0.9897	0.262			0.9914	0.258
D_4	390.6	$> 2.26\times10^{77}$	0.9934	0.223	409.6	$> 8.77\times10^{89}$	0.9951	0.207
A_1			0.9797	0.161			0.9820	0.164
$A_{1.5}$	53.2	9.24×10^{13}	0.9962	0.022	54.4	3.02×10^{14}	0.9985	0.015
A_2			0.9963	0.038			0.9985	0.020
A_3			0.9964	0.045			0.9985	0.038
A_4			0.9965	0.135			0.9986	0.091
R_2			0.9907	0.125			0.9925	0.122
R_3	198.1	1.03×10^{69}	0.9933	0.111	203.5	5.25×10^{68}	0.9951	0.103
P_1			0.9797	0.161			0.9828	0.164
P_2			0.9791	0.088			0.9815	0.082
P_3			0.9784	0.053			0.9809	0.054
P_4	38.7	4.65×10^{8}	0.9777	0.040	39.1	2.28×10^{9}	0.9803	0.041
C_1	220.8	$> 2.26\times10^{77}$	0.9964	0.098			0.9986	0.061
$C_{1.5}$			0.9899	0.210			0.9953	0.153
C_2			0.9950	0.114	264.8	$> 8.77\times10^{89}$	0.9993	0.049
Au	52.1	5.45×10^{-20}	0.2408	0.993	47.1	1.27×10^{-16}	0.2461	0.952

low temperature follow the law

$$f(\alpha) = 1.5(1 - \alpha)[-\ln(1 - \alpha)]^{1/3} \qquad (2)$$

and that a nucleation-growth process occurs with $n = 1.5$. Moreover, it can be calculated that $E = 53.0$ kJ mol^{-} and that $A = 1.2 \times 10^{14}$.

These results agree with conclusions reached by other authors [1,8], who have researched the martensitic phase transition for similar systems by other methods. It can be seen that DSC analysis is still an important means of studying martensitic transition kinetics in an alloy. However, the present method has a series of advantages including convenience, rapidity, and less sample weight required.

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REFERENCES

1 Zuyao Xu, Martensitic Transformation and Martensite, Science Press, Beijing, 1980 (in Chinese).
2 Jianchun Li and G.S. Ansell, Metall. Trans. A, 14 (1983) 1293.
3 W. Gutt and A.J. Majumdar, in R.C. Mackenzie (Ed.), Differential Thermal Analysis, Vol. 2, Academic Press, London, 1972, Chapter 29.
4 J. Perkins and W.E. Muesing, Metall. Trans. A, 14 (1983) 33.
5 J. Beyer, P.A. Besselink and A.J. Aartsen, Thermochim. Acta, 85 (1985) 187.
6 J. Sestak, Non-isothermal kinetics, in H.G. Wiedemann (Ed.), Thermal Analysis, Proc. 3rd ICTA, Birkhauser Verlag, Basel, 1972, Vol. 2, p. 3.
7 R.B. Shannon, Trans. Faraday Soc., 60 (1964) 1902.
8 R. Pati and M. Cohen, Acta Metall., 17 (1969) 189.