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The growth characteristics of single crystals with a shape memory effect

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Abstract. Using the Bridgman technique, the growth characteristics of single crystals with a shape memory effect have been studied in detail. The experimental results show that there is a critical growth velocity for the chosen material. If the growth velocity is below this critical value, then a single crystal can be grown—otherwise a polycrystal will be formed; the critical growth velocity is dependent on (i) the diameter of the grown crystal, (ii) the purity and form of the raw materials used, and (iii) the temperature gradient in the oven used for single-crystal growth. An empirical formula is proposed for those dependences. Good homogeneous single crystals with carefully controlled compositions can be obtained by choosing suitable growth parameters, in particular, an appropriate growth velocity.

1. Introduction

The shape memory effect has been found in many alloys. It is described as the ability of some materials to be deformed below certain temperatures and then to return to their original shape upon heating. The three major types of technologically applicable shape memory alloys which can be used as thermomechanical devices are CuZnAl, CuAlNi, NiTi. More and more researchers are interested in the development of copper-based shape memory alloys due to their lower cost and simple fabrication. The measurement of their properties as single crystals provides information on the mechanism of the thermoelastic behaviour [1]. However, as far as we know there is no published paper of systematic research on the growth of single crystals with a shape memory effect except for a Letter to the Editor [2].

The growth characteristics of single crystals with shape memory have been systematically studied in this paper.

2. Experimental procedure

In order to obtain a single crystal in which the composition is uniform we produced a polycrystal under argon atmosphere from the raw materials. Three kinds of copper were chosen for our experiments; their purities were 99.7%, 99.9%, 99.999%

Table 1. The different values of β for three kinds of copper and the measured critical growth velocity (mm h^{-1}).

No	Size of raw material copper	Purity α	$1/a$ (mm)	β (mm)	V_c (mm h^{-1})
1	Shot 1–8 mm	0.999	1.50	4.50	5.0
2	Cylindrical 27 ^a 51.6 mm ²	0.997	5.35	13.50	15.0
3	Cylindrical 15 ^a 166.5 mm ²	0.99999	3.44	17.20	20.0

^a All the diameters of the grown crystals are 20 mm and \bar{G} is kept at 10 K cm^{-1}

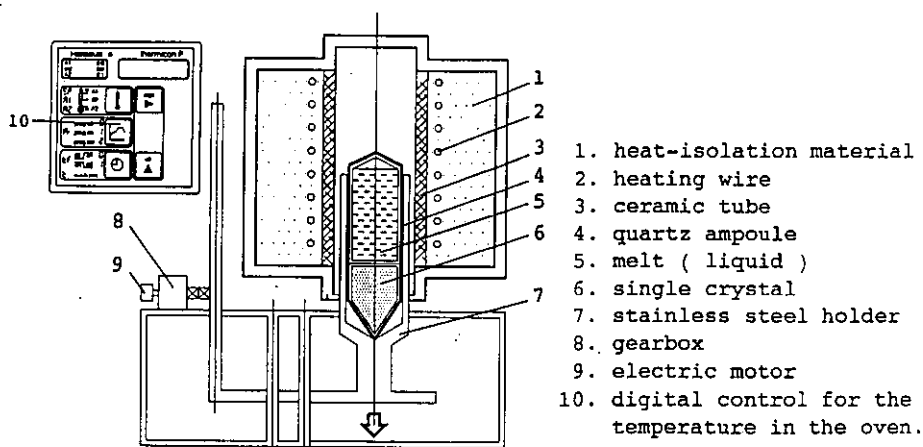


Figure 1. The schematic diagram of the Bridgman growth device for single crystals with shape memory.

respectively (see table 1). The purities of the zinc, aluminium and nickel used were respectively 99.99%, 99.9% and 99.9%.

The device for single-crystal growth is shown in figure 1. The oven and its temperature control were made by the Heraeus Company in Germany. The crucibles used for the growth of CuAlNi and CuZnAl were respectively graphite and quartz ampoules which were sealed in argon atmosphere. The moving velocities of the crucibles could be changed from 0.2 mm h^{-1} to 40 mm h^{-1} .

The shape memory alloys in the experiments were Cu-14.0Al-4.0Ni , Cu-18.5Zn-7.0Al and Cu-20.0Zn-6.0Al (wt%).

3. Experimental results

3.1. The temperature distribution in the oven

The measured temperature distribution $T = T(L)$ is shown in figure 2 for a central

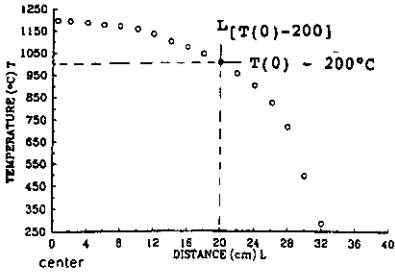


Figure 2. The temperature distribution in the oven when the temperature at the centre is 1200 °C.

temperature of $T(0) = 1200\text{ °C}$. The average temperature gradient is defined as

$$\bar{G} = \frac{T(0) - (T(0) - 200\text{ °C})}{L_{[T(0)]} - L_{[T(0)-200]}}$$

Hence $\bar{G} = 10\text{ K cm}^{-1}$ in figure 2.

The central temperature is generally chosen to be 100 K higher than the melting point T_m . For CuAlNi and for CuZnAl T_m is 1100 and 1000 respectively. For both alloys \bar{G} is about 10 K cm^{-1} .

3.2. The effect of the moving velocity of the crucible

The relation between the moving velocity V_m of the crucible and the number of grains in the grown CuAlNi crystals is shown in figure 3. We can see that if the moving velocity of the crucible is greater than a specific value, called V_c , polycrystals appear. Otherwise single crystals can be obtained.

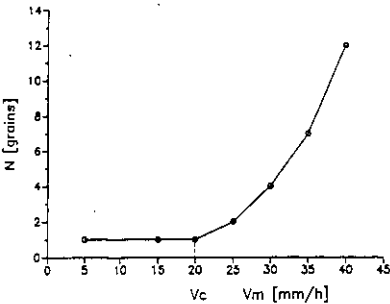


Figure 3. The relation between the moving velocity of the crucible and the number of grains in the CuAlNi crystals ($\bar{G} = 10\text{ K cm}^{-1}$).

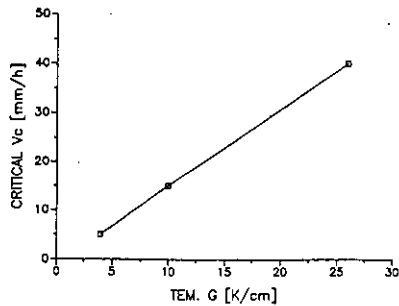


Figure 4. The relation between the critical growth velocity V_c and the average temperature gradient \bar{G} in the oven for CuAlNi crystals.

3.3. The effect of the temperature gradient

The relation between the critical growth velocity V_c and the average temperature gradient \bar{G} is shown in figure 4. It is found that the critical growth velocity is higher for a larger temperature gradient in the oven. Therefore single-crystal growth becomes easier for bigger gradients.

3.4. The effect of the radius of the crystal

For bulk crystal growth, it is well known that growth of a big crystal is more difficult than growth of a small crystal. The experimental results for the growth of CuZnAl crystals is shown in figure 5. As we can see, the smaller the radius r of the grown crystals, i.e. the greater the value $2/r$, the higher the critical growth velocity V_c . There is an approximately linear relation between the critical growth velocity V_c and the value of $2/r$. The reason for this needs to be investigated further.

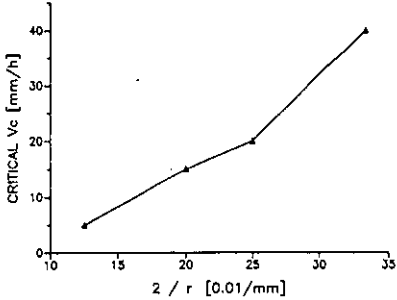


Figure 5. The relation between V_c and the value $(2/r)$ for growth of CuZnAl crystals ($\bar{G} = 10 \text{ K cm}^{-1}$).

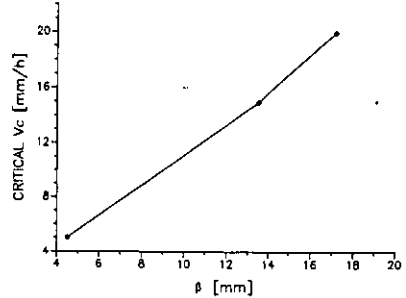


Figure 6. The relation between β and the critical growth velocity V_c for the growth of CuZnAl crystals ($\bar{G} = 10 \text{ K cm}^{-1}$). See text for the definition of β .

3.5. The effect of the quality of raw materials

The experimental results show that both the purity and granularity, and the shapes of the raw material, have a direct effect on the presence of oxides in the polycrystal from which the single crystal is grown. Therefore, there is a direct relation between the quality of raw materials (their purity and shape) and single-crystal growth. The smaller the size of raw material, the more oxides will be formed during the process. These oxides may also become heterogeneous crystal nuclei, i.e. seeds, during the later crystal growth process, because their melting points are much higher than those of the pure metals or alloys. From our experiments, both of these factors can be summarized into one effective parameter, the coefficient of raw material, defined by

$$\beta = (1/a) \log[1/(1 - \alpha)].$$

Here α is the purity of the copper used; V_{sum} and A_{sum} are its total volume and its total surface respectively; $A_{\text{sum}}/V_{\text{sum}}$ can be defined as its specific surface a . The experimental results for CuZnAl alloys with three different kinds of copper are shown in table 1. The relation between β and the critical growth velocity V_c for CuZnAl crystal growth is shown in figure 6. The experimental results in table 1 and figure 6 show that the high purity and big size of raw materials are favourable for single-crystal growth.

3.6. The relation between the growth parameters and the properties of the grown crystals

The uniformity of composition in the grown crystal is very important for its properties. But it is not easy to measure the composition distribution in the grown crystal.

Nevertheless we can determine the uniformity of composition in the grown crystal roughly by measuring differences in its martensite starting temperature M_s between the ends of the sample, since there is a linear relation between the solute composition (Ni, Zn, Al) and M_s [4]. The shape of the samples used for this measurement is shown in figure 7(a). The sample was cut from a single crystal of diameter 6 mm. This diameter permits growth velocities in the range 1.875–40 mm h⁻¹. The head and tail of the grown crystal were cut off at a length of 20 mm, because we expect strong non-uniformities of composition at those extremities. The cooling rate of the sample during the measuring process was 0.5 °C min⁻¹. The size of the tested samples is 80 mm × 6 mm × 2 mm. The temperature difference of the martensitic transformation between the ends of the measured sample is denoted by

$$\Delta M_s = M_{s1} - M_{s2} \text{ (}^\circ\text{C)}.$$

The relation between various growth velocities (V_g) and the measured temperature differences ΔM_s of the martensitic transformation is shown in figure 7(b). The experimental results show that for small growth velocities, the value of ΔM_s will decrease with an increase of the growth velocity, i.e. the composition distribution in the grown crystal becomes more uniform for large velocities. But there is a critical value, here 15 mm h⁻¹ for CuZnAl; when the growth velocity is above this value, the ΔM_s will always be zero in the range of the measuring error (about 1 °C in the experiment) even if the growth velocity is further increased.

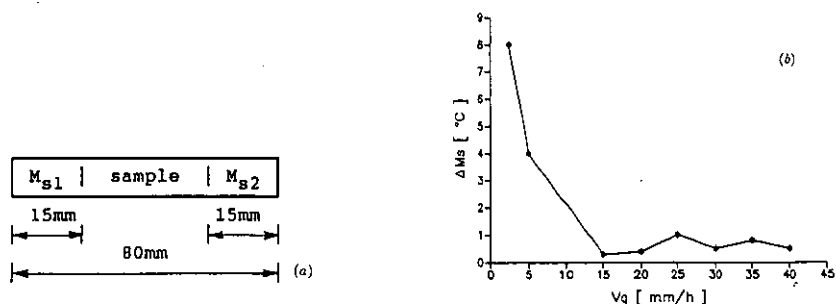


Figure 7. (a) The schematic diagram of the sample for ΔM_s measurement. (b) The relation between the growth velocity V_g and ΔM_s for the growth of CuZnAl crystals ($\bar{G} = 10 \text{ K cm}^{-1}$).

The stress–strain curve for a uniform CuZnAl single crystal with $M_s = 5 \text{ }^\circ\text{C}$ is shown in figure 8. The measuring temperature is 38 °C, the loading rate is 0.06 mm min⁻¹. The changes between austenite and martensite during the loading and unloading processes are shown in figure 9. The current CuZnAl single crystals show horizontal yield and recovery lines during the phase transformations. Previously used CuZnAl single crystals [2] seem to be homogeneous in composition, but their stress–strain curves do not have horizontal parts. This difference is understandable from [4]:

$$M_s \text{ (K)} = 3280 - 80C_{\text{Zn}} - 110C_{\text{Al}}$$

where C_{Zn} and C_{Al} are the compositions (wt%) of Zn and Al respectively in the CuZnAl single crystal. It can be seen that even a small difference of solute distribution in the single crystal can make a big difference in its martensitic transformation

temperature M_s . Therefore, the ordinary method of compositional analysis is not suitable for the analysis of the compositional uniformity in crystals with a shape memory effect.

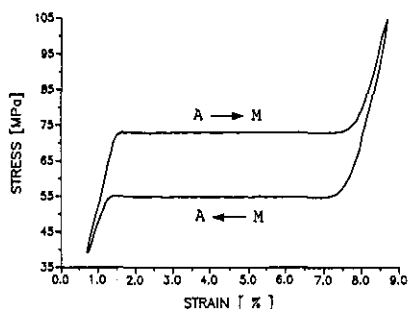


Figure 8. The stress-strain curve of the uniform CuZnAl single crystal.

The good homogeneity of the solute in our grown crystals can be attributed to (i) the homogeneous polycrystals used for single-crystal growth; (ii) the sealing of the quartz ampoules under argon atmosphere; this prevents zinc from evaporating.

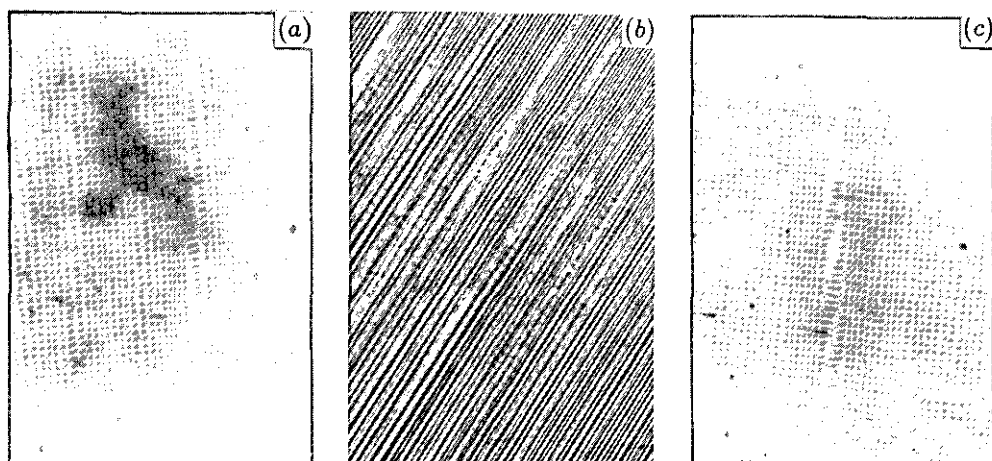


Figure 9. The change between austenite and martensite. (a) 100% austenite. (b) austenite + martensite. (c) 100% martensite.

4. Discussion

4.1. The energy equilibrium in the growth process

Following [3], we balance the energy in a small closed zone, see figure 10, along the crystal growth direction and obtain

$$Lm = Ak_s G_s - Ak_l G_l. \quad (1)$$

Here L is the latent heat of solidification and \dot{m} is the mass solidifying per unit time. $k_{s,l}$ are the heat conductivities in the two phases and $G_{s,l}$ corresponding temperature gradients. Since $\dot{m} = \rho_s A V_g$ we have

$$V_g = (k_s G_s - k_l G_l) / \rho_s L. \quad (2)$$

4.2. An estimate of the critical growth velocity

From the experimental results in section 3 we propose the following empirical formula for the critical growth velocity

$$V_{cg} = u(2/r)\beta V_g$$

or with (2)

$$V_{cg} = u(2\beta/rL\rho_s)(k_s G_s - k_l G_l). \quad (3)$$

Here $2/r$ determines the diameter of the crystal; $\beta = (1/a) \log[1/(1 - \alpha)]$ is the effective parameter of the raw materials, and u is a material coefficient related to the surface tension of the melt and the properties of the raw solute materials (Zn, Al and Ni).

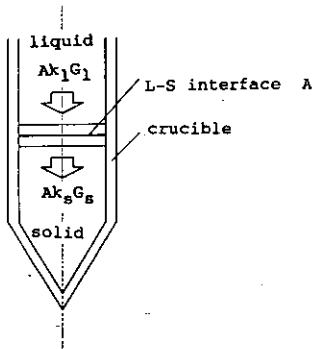


Figure 10. The energy equilibrium in l-s interface.

Since G_l is much smaller than G_s which is nearly equal to \bar{G} , equation (3) can also be written as

$$V_{cg} \simeq u \frac{2}{r\rho_s L} \beta k_s G_s \simeq u \frac{2\beta k_s \bar{G}}{r\rho_s L}. \quad (4)$$

We proceed to determine the approximate value of u from our experimental results. For the material parameters k_s , ρ_s and L we choose the values of Cu, since this is the major constituent

$$\rho_s = 8.89 \text{ g cm}^{-3} \quad k_s = 385 \text{ W mK}^{-1} \quad L = 214 \text{ J g}.$$

From figure 5, if $r = 8 \text{ mm}$, then $V_c = 20 \text{ mm h}^{-1}$ with $\beta = 13.5 \text{ mm}$; this gives $u = 0.081$.

The calculated values and experimental values for V_{cg} and V_c from table 1 are shown in table 2. We can see good agreement between the experimental values V_c and theoretical calculations of V_{cg} . We consider this as support for the proposed empirical relation (3).

Table 2. The calculated and experimental values of the critical growth velocity of the CuZnAl single crystals.

No	Calculated values					
	$2r$ (mm)	β (mm)	$2\beta/r$	V_g (mm h ⁻¹)	V_{cg} (mm h ⁻¹)	V_c (mm h ⁻¹)
1	20	4.5	0.90	72.84	5.31	5.0
2	20	13.5	2.70	72.84	16.09	15.0
3	20	17.2	3.44	72.84	20.03	20.0

5. Conclusions

There is a critical growth velocity for the chosen material (CuZnAl and CuAlNi). If the growth velocity is below this critical value, then a single crystal can be grown—otherwise a polycrystal will be formed; the critical growth velocity is dependent on: (i) the diameter of the grown crystal; (ii) the purity and shape of the raw material used; (iii) the temperature gradient in the oven. An empirical formula has been proposed for these relations.

Good homogeneous single crystals with carefully controlled composition can be obtained by choosing suitable growth parameters. The best crystal-growth velocities for Cu-based alloys (CuZnAl and CuAlNi) with diameters of 16 and 20 mm are 20 and 15 mm h⁻¹ respectively if the average temperature gradient near to their melting points in the oven used is about 10 K cm⁻¹.

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