Parameters of Martensite Transformation and Structural State in Rapidly Quenched Ti35Ni15Cu Shape Memory Alloys

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Abstract. Influence of the quenching rate on the martensite transformation parameters (transformation temperatures and hysteresis) of 50Ti35Ni15Cu shape memory ribbons obtained by meltspinning technique has been studied. Increase of quenching rate results in decrease of the $B2 \rightleftharpoons B19$ and $B19 \rightleftharpoons B19'$ martensite transformations temperatures, broadening of direct and reverse transformation intervals, decrease of hysteresis. The B2-type ordering takes place during rapid solidification. Rapid solidification of 50Ti35Ni15Cu alloy results in fine β -phase grain size structure with relative large size scattering. Two types of martensite morphology, plate-like and triangular shapes, have been observed in ribbons.

1. INTRODUCTION

Variation of the shape memory alloys chemical composition, preliminary plastic deformation, thermal and thermomechanical treatment is traditionally effective way to manage the martensite transformation parameters (namely, transformation temperatures and hysteresis), physical and mechanical properties caused by the martensite transformations.

Recently great attention is paid to development of relatively new casting technique as rapid quenching from liquid phase. High quenching temperature rates (10^4 - 10^7 K/s) allow one to receive material with unusual structure - fine grain size or amorphous one - and changed mechanical properties [1-5]. In ribbons the martensite transformation temperature range is shifted with respect to one taking place in bulk material. Martensite plates have specific morphology. Mechanical properties are also changed as compared with those in bulk material. Large part of experimental data concerning study of rapidly quenched ribbon structure has been obtained on the TiNi-based SMA's in which Cu (up to 25 at.%) was added instead of Ni. There are several works related to study of the parent and martensite phases structure in rapidly quenched TiNi-based alloys [6,7].

So, from one hand, the TiNi-based SMA's are widely used in practice and the traditional schedule of the alloy casting, cold/hot working and thermal treatment are well developed but new properties and new application fields can be expected for non-conventional production technique - melt spinning or rapid solidification from liquid phase. From another hand, use of the melt spinning technology for SMA's production is not yet sufficiently studied and effect of the technology parameters (quenching rate, overheating above liquid solution temperature, ribbon thickness) on the parent and martensite phase structure, transformation temperatures and shape memory parameters is not well studied.

This work presents experimental results related to the effect of quenching temperature rate on the direct and reverse martensite transformation temperatures, transformation intervals and hysteresis, the parent phase and martensite microstructure of Ti35Ni15Cu meltspinning ribbons.

2. MATERIAL AND TECHNIQUES

Details of the meltspinning technique for ribbon production are presented elsewhere [1]. Short version of production technique specific for chosen Ti35Ni15Cu alloy is given below. Initial alloy ingot (50 g by

weight) was prepared by arc-melting technique in vacuum or inert gas atmosphere from iodide titanium (purity 99,8%) and electrolytic nickel (99,99%) and copper (99,99%). To achieve good homogeneity the ingots were three-times remelt, ingot final chemical composition was 49.723Ti-35.258Ni-15.019Cu (at.%) according to chemical analysis. Then ingot was cut in three parts, each part remelt in high frequency magnetic levitation inductor and put on outer side of rotated copper wheel (refrigerator). Quenching rate was varied from 10^4 up to 10^7 K/s by changing the wheel angular speed. The thickness of ribbons was near 120 microns for 10^4 K/s, 60 microns for 10^5 K/s and 35 microns for 10^6 K/s.

Transformation temperatures were determined from the resistance versus temperature curves obtained by using special equipment. These measurements were performed in 77K - 800K temperature range under continuously varying temperature regime with cooling rate 0.2-10K/s and heating rate 0.2-20K/s. Microstructure of high temperature (β , bcc) phase and martensite phases was studied by means of metallography (MIM-8) and transmission electron microscopy (Tesla).

3. EXPERIMENTAL RESULTS AND DISCUSSION

The resistance versus temperature curves for 50Ti35Ni15Cu melt spinning ribbons are shown in fig. 1 for quenching rates 10^4 K/s (a), 10^5 K/s (b) and 10^6 K/s (c), respectively. Two regions of the resistance anomaly associated with two martensite transformations are observed: $B2 \Rightarrow B19$ ($M_{s1}-M_{f1}$) and $B19 \Rightarrow B19'$ ($M_{s2}-M_{f2}$) on cooling and reverse sequence $B19' \Rightarrow B19$ ($A_{s2}-A_{f2}$) and $B19 \Rightarrow B2$ ($A_{s1}-A_{f1}$) on heating. These two transformations are separated by definite temperature interval that becomes narrower with increase of quenching temperature rate. It is seen that transformation temperatures also shift to lower temperatures. Hysteresis of martensite transformations measured as a temperature interval between 50% of new phase formation also changes specifically. Variations of these parameters are presented in fig. 2 and 3. Hysteresis of the $B2 \rightleftharpoons B19$ transformation remains near 12K for temperature rates 10^4 - 10^5 K/s and decreases a little for 10^6 K/s, while hysteresis of the $B19 \rightleftharpoons B19'$ transformation decreases significantly from 16K to 6K in 10^4 - 10^5 K/s temperature rate interval and only small variation occurs at higher temperature rates. This difference in hysteresis behaviour for two transformations may be caused by difference in the martensite phases microstructure, crystal size and "perfectness" of the martensite/martensite boundaries.

Table 1.

		B2 $\rightleftharpoons$ B19								B19 $\rightleftharpoons$ B19'							
QTR	Ribbon	M_s^1	M_f^1	ΔM^1	A_s^1	A_f^1	ΔA^1	$\Delta T^{50\%}$		M_s^2	M_f^2	ΔM^2	A_s^2	A_f^2	ΔA^2	$\Delta T^{50\%}$	
K/s	thickness microns	----- K -----								-----							
10^4	115	336	308	28	328	348	20	12		235	189	46	187	247	54	16	
10^5	40	326	304	22	325	353	28	13		208	148	60	148	213	65	6	
10^6	35	319	280	39	293	329	36	10		198	153	45	163	213	50	4	

There exists also a difference in variation of the $B2 \rightleftharpoons B19$ and $B19 \rightleftharpoons B19'$ martensite transformation temperatures with increase of temperature rate from 10^4 to 10^6 K/s (see fig. 3 and Table 1). Qualitative explanation of this effect can be given taking into account different nature of the "initial conditions": the first occurs from parent β phase containing thermal stresses while second is the martensite-martensite transformation from state with high defect density.

Let us consider regularity of ribbon microstructure formation at different temperature rates. Metallography measurements showed fine grain size of the β phase and its considerable scattering with

increase of temperature rate. Dispersion in grain size can result in widening of the direct and reverse transformation temperature ranges, namely M_s - M_f and A_s - A_f intervals.

Both small grain size and its dispersion are confirmed by the TEM/SAD studies. Relatively large grains (>10 microns) are observed in ribbons prepared with temperature rate 10^4 K/s. SAD patterns taken in such grains are typical single crystal set (see SAD in fig. 4a, foil orientation $[011]_\beta$). Despite high quenching temperature rates the B2-type ordering took place in β phase. Indeed, SAD patterns contain $\{100\}_\beta$, $\{111\}_\beta$ and others superstructure reflections.

Decrease of the β phase grain size with quenching rate results in specific changes of SAD patterns - there appear diffraction circles in addition to definite point reflection sets. Finally diffraction circles become continued and radial spread (fig. 4b) at temperature rate near 10^6 K/s. Possible reasons of such diffraction circles broadening are high thermal stresses level in thin ribbons and geometrical effect for grain size less than 1 micron.

Several general features were found with effect of quenching temperature rate on the martensite phase microstructure formed during rapid solidification or during cooling ribbon to lower temperatures.

Usually the thermoelastic martensite in TiNi based SMA's has plate-like morphology and linear size of plates is varied with temperature or stress applied. Rate of martensite plate size change is a function of overcooling degree below M_s , cooling/heating rate and stress level.

Alloying of TiNi by Cu leads to significant change in the martensite morphology. In addition to plate-like martensite there appears areas with triangle morphology (fig. 5). Volume ratio between two types morphologies depends on quenching temperature rates. For low temperature rates (10^4 K/s) the dominant martensite crystal morphology is triangular shaped one. For temperature rates near 10^5 K/s volume ratio between plate-like and triangle-shaped morphologies becomes close to 1:1. For higher quenching rate (10^6 K/s) the predominant martensite crystal morphology is plate-like one but size of plates becomes smaller.

Attempt to find correspondence between two $B2 \rightleftharpoons B19$ and $B19 \rightleftharpoons B19'$ martensite transformations and two types of martensite morphology in Ti35Ni15Cu alloy does not give positive result.

4. CONCLUSIONS

1. Influence of the quenching rate on the martensite transformation parameters (transformation temperatures and hysteresis) of 50Ti35Ni15Cu shape memory ribbons obtained by meltspinning technique has been studied. Increase of quenching rate results in decrease of the $B2 \rightleftharpoons B19$ and $B19 \rightleftharpoons B19'$ martensite transformations temperatures, broadening of direct and reverse transformation intervals, decrease of their hysteresis.
2. Despite high quenching rates the B2-type ordering takes place during rapid solidification.
3. Rapid solidification of 50Ti35Ni15Cu alloy results in fine β -phase grain size structure with relative large size scattering.
4. Two types of martensite morphology, namely plate-like and triangular shapes, have been observed in rapidly quenched 50Ti35Ni15Cu shape memory ribbons.

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Figure 1: Electrical resistance versus temperature dependencies: 10^4 K/s (a), 10^5 K/s (b), 10^6 K/s (c).

Figure 2: Transformation temperatures versus quenching rate for $B2 \rightleftharpoons B19$ and $B19 \rightleftharpoons B19'$

Figure 3: Hysteresis variation with quenching rate for $B2 \rightleftharpoons B19$ and $B19 \rightleftharpoons B19'$ transformations

Figure 4: Two types of SAD patterns: 10^4 K/s (a), 10^5 K/s (b).

Figure 5: Plate and triangular martensite morphology for 10^4 K/s (a), 10^5 K/s (b) and 10^6 K/s (c). x500.

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