Crystallization in Partially Amorphous $\text{Ni}_{50}\text{Ti}_{32}\text{Hf}_{18}$ Melt Spun Ribbon

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A partially amorphous $\text{Ni}_{50}\text{Ti}_{32}\text{Hf}_{18}$ melt spun ribbon has been characterized by means of calorimetry, X-ray diffraction and transmission electron microscopy, showing that the amorphous regions are mostly concentrated in the wheel side as a consequence of a higher cooling rate during the fast solidification (*i.e.* higher solidification rate). Special emphasis has been given to the crystallization process of the amorphous regions, studying the evolution of the microstructure and the martensitic transformation. Although several crystallization procedures have been carried out by thermal treatments, either slightly under or over the crystallization temperature measured by DSC, T_C , the final microstructure and calorimetric behavior of the fully crystalline samples does not depend on the applied temperature. The fully crystalline samples contain regions with small crystallites produced during the thermal treatment (showing that the crystal nucleation energy is rather low for this alloy) together with the large crystals originated during the melt-spinning. At room temperature (RT), both types of crystals are in martensitic state. The new crystallized regions with small grain size show notably lower transformation temperatures and higher hysteresis in comparison to the big crystals already existing before the crystallization treatments. However, an additional mechanism, apart from the crystal size, affects the transformation temperatures, likely related to the presence of more defects (mainly grain boundaries) in the crystallites created by thermal treatments. These defects could act as nucleation sites for the martensite and increase the transformation temperatures with respect to the as cast spherical crystallites of similar sizes.

(Received December 22, 2003; Accepted April 5, 2004)

Keywords: crystallization, melt-spinning, nickel titanium based alloys, martensitic transformation

1. Introduction

The use of new techniques to produce shape memory alloys (SMA) by means of alternatives to conventional casting, like rapid solidification by melt-spinning, has received increasing attention in recent years. With this technique, almost ready-to-use ribbons can be produced avoiding complex thermomechanical treatments. However, important microstructural and functional changes are introduced in comparison to the conventionally cast materials, as the reduction of the grain size¹⁾ and the decrease of the transformation temperatures.^{2,3)} Many parameters during the casting by melt spinning play an important role in the quality of the final product, several of them affecting directly the solidification rate of the melt and, then, the grain size (the faster the solidification occurs the finer the grain size is);¹⁾ even amorphous material may be produced by this technique when the solidification rate is high enough. In fact, the relative easiness to produce amorphous alloys by melt-spinning makes this technique one of the most widely used methods for casting metallic glasses with ribbon shape.

Production of amorphous material may seem useless in the field of SMA, as it requires a subsequent crystallization process in order to obtain the martensitic transformation. However, the exceptional ductility of amorphous alloys can be used for shaping the materials, which will exhibit shape memory properties after crystallization. Moreover, by modifying the crystallization parameters, it might be possible to control the final microstructure, and thus some properties of the martensitic transformation and related functional properties. First works on this new attractive idea have been carried out mainly in $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$.^{4,5)} In addition to that, further investigations have also been performed on initially (partially) amorphous^{6–10)} or crystallized^{11–13)} $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ ribbons. On the other hand, most investigations on the crystallization

of Zr-Ti-Ni based alloys have been performed away from compositions giving martensitic transformation (see Inoue¹⁴⁾ for a general overview about bulk metallic glasses). Amorphous Ni-Ti-Hf alloys can also be obtained by melt-spinning and first results after crystallization have been reported on an alloy from this family by Dalle *et al.*¹⁵⁾

Conventionally cast Ni-Ti-Hf alloys are well known for their high martensitic transformation temperatures when Hf exceeds 10 at%.^{16,17)} Despite the reduction of the transformation temperatures with respect to the bulk alloy, melt spun Ni-Ti-Hf ribbons still may show high transformation temperatures.^{18,19)} In Santamarta *et al.*¹⁸⁾ and Cesari *et al.*,¹⁹⁾ a completely crystalline as cast $\text{Ni}_{50}\text{Ti}_{32}\text{Hf}_{18}$ ribbon and its evolution under thermal treatments in martensite and in austenite, respectively, has been already characterized.

In the present contribution, an extensive characterization of a partially amorphous $\text{Ni}_{50}\text{Ti}_{32}\text{Hf}_{18}$ melt spun ribbon has been performed by means of differential scanning calorimetry (DSC), X-ray diffraction (XRD) and transmission electron microscopy (TEM). Special emphasis has been given to study the crystallization process of the amorphous regions by different thermal treatments above and below the crystallization temperature measured by DSC, T_C , as well as the evolution of its microstructure during these processes.

2. Experimental Procedure

A $\text{Ni}_{50}\text{Ti}_{32}\text{Hf}_{18}$ ribbon was prepared under helium atmosphere by planar flow casting from conventionally produced ingots of the same composition. The ingots were molten under He atmosphere and ejected at 200 hPa onto a rotating wheel with a surface speed of 19 m/s, producing a metallic ribbon ~30 μm thick and 9.5 mm wide.

Calorimetric measurements were performed in a Perkin Elmer DSC-7 working between 235 and 875 K. A rate of

0.33 K/s was used in most of the runs, as in the measurement of the crystallization temperature (T_C). Faster runs at ~ 3.3 K/s up to 755 or 775 K with subsequent plateaus at those temperatures were also used for the crystallization experiments below T_C . Other samples were completely crystallized over T_C , either by fast runs in the DSC up to 875 K followed by rapid cooling to room temperature (RT) or by upquenching in a salt bath at 835 K during 1 minute.

X-ray diffraction (XRD) patterns were carried out at RT in a θ - 2θ Bragg-Brentano configuration using a Siemens D5000 system (Cu- K_α radiation) equipped with a scintillation detector. Diffraction patterns taken at higher temperatures were performed under a θ - θ configuration in a similar device equipped with a controlled temperature chamber and a position sensitive detector.

Observations by transmission electron microscopy (TEM) were carried out in a Hitachi H-600 operating at 100 kV equipped with double-tilt holder and energy dispersive X-ray (EDX) spectrometer; heating and cooling single tilt holders were also used for *in-situ* experiments. Samples for TEM were obtained from 3 mm discs by double-jet electropolishing at ~ 15 V and 240 K using a solution of 30% nitric acid in methanol.

3. Results

3.1 Differential scanning calorimetry

DSC measurements performed to as cast samples in order to check the presence of martensitic transformation exhibit one single peak during cooling and heating between 235 and 575 K. The peak temperatures during the forward and reverse transformation are around 440 and 510 K, respectively, with an enthalpy change of 7 J/g (Fig. 1(a)). The latter value is rather low in comparison to a completely crystalline melt-spun ribbon with the same nominal composition, which showed an enthalpy change slightly higher than 20 J/g.¹⁹⁾ The presence of amorphous regions in the ribbon, as it will be confirmed in next sections by means of direct methods like XRD and TEM, leads to this low enthalpy change.

In order to obtain fully crystalline samples and determine the temperature at which the crystallization occurs, heating runs up to 875 K have been performed in the calorimeter at

0.33 K/s, resulting in a crystallization temperature, T_C , of 793 K. After the crystallization runs, a martensitic transformation split in two important calorimetric peaks (with a total enthalpy change slightly lower than 20 J/g) has been detected (Fig. 1(b)).

Other crystallization processes involving thermal treatments over T_C (e.g. fast heating runs in the DSC up to 875 K at 3.3 K/s or upquenching into a salt bath at 835 K for 1 minute), have been carried out in order to observe possible differences on the thermal behavior of the subsequent martensitic transformation. However, the specimens after any of these three crystallization processes show very similar qualitative and quantitative calorimetric results.

Finally, in order to characterize the evolution in the ribbon after a gradual crystallization at temperatures slightly under T_C , thermal treatments at 755 and 775 K in series of increasing times have been carried out. After each step of the progressive crystallization, the martensitic transformation has been controlled by DSC runs between 235 and 575 K (temperatures far below from T_C). The evolution of the martensitic transformation is quite similar for both temperatures of thermal treatment, apart from an evident shift to lower times for the 775 K series with respect to the 755 K one. Figure 2 shows that the thermograms from the direct and reverse transformations performed after the shortest times of the series at 775 K are quite similar to the ones obtained in the as cast ribbon, except for a second and broad calorimetric peak at lower temperatures shown by the annealed ribbon. An additional peak arises at lower temperatures when increasing the holding time at 775 K, approaching to the peaks at higher temperatures at the end of the crystallization series. This third peak exhibits a high value of the enthalpy change, which increases the total energy of the transformation close to the values reported on a fully crystalline sample with the same composition.¹⁹⁾

3.2 X-Ray diffractometry

X-ray diffraction patterns have been obtained at room temperature (RT) on both sides of the as cast ribbon. The side that solidifies in contact with the wheel during the melt-spinning will be referred hereafter as “wheel side”, whereas the opposite one will be notated as “free side”. Despite using the same parameters for both sides, the diffraction patterns in the wheel side (Fig. 3(a)) reveal a broad peak around 40° in 2θ , confirming the existence of amorphous regions, while it is almost indistinguishable in the free side (Fig. 3(b)). Furthermore, Fig. 3(b) exhibits higher intensities for the sharp peaks (corresponding to the crystalline phases). These results indicate that the amorphous zones existing in the as cast ribbons are mainly located near the wheel side.

Quantitative analyses of the X-ray spectra for the present ribbon worked out a lattice parameter of $a = 0.307$ nm for the cubic (B2) austenite. The crystalline peaks that do not match with the cubic structure can be fitted with a monoclinic B19' martensite with the following lattice parameters: $a = 0.304$ nm, $b = 0.406$ nm, $c = 0.483$ nm and $\beta = 102.8^\circ$. Similar results have been obtained for a series of $\text{Ni}_{50-x}\text{Ti}_{32}\text{Hf}_{18}\text{Re}_x$ ribbons, with x between 0 and 2.0 at%,²⁰⁾ confirming that the density of amorphous regions is again higher in the wheel side than in the free side. Moreover, the intensity of the

Fig. 1 Thermal cycles performed in the DSC for the $\text{Ni}_{50}\text{Ti}_{32}\text{Hf}_{18}$ in the as cast state (a) and after a crystallization process in the DSC up to 875 K (b).

Fig. 2 Evolution of the direct (a) and reverse (b) transformation of the $\text{Ni}_{50}\text{Ti}_{32}\text{Hf}_{18}$ during the controlled crystallization consisting of heat treatments at 775 K during different times.

Fig. 3 X-ray diffraction patterns corresponding to the wheel (a) and free (b) sides for the as cast $\text{Ni}_{50}\text{Ti}_{32}\text{Hf}_{18}$ ribbon.

peaks from austenite in relation to those from martensite is also higher in the wheel side.²⁰⁾

Additional X-ray diffraction patterns have been recorded as a function of the temperature for samples previously crystallized during 1 minute in a salt bath at 835 K. During heating, diffraction patterns have been obtained at RT, 425 K and 525 K (*i.e.* just before, in the middle of the two calorimetric peaks and at the end of the reverse transformation, respectively-*Fig. 1(b)*). Following the same criteria for the forward transformation upon cooling, the measurements have been done at 375 K and RT, respectively. Figure 4 shows an angular region of the corresponding

Fig. 4 Detail of five X-ray diffraction patterns taken at different temperatures for the crystallised $\text{Ni}_{50}\text{Ti}_{32}\text{Hf}_{18}$ ribbon. Upon heating (a) was taken at RT; (b) at 425 K and (c) at 525 K; upon cooling (d) was taken at 375 K and (e) at RT. The reflections corresponding to both crystalline phases are also detailed; the peak labelled as "Pt" is produced by the sample holder of the diffractometer.

diffractograms containing peaks from both phases (*i.e.* austenite and B19' martensite). Upon heating, the 002_{mart} and $\bar{1}11_{\text{mart}}$ peaks vanish instead of the 110_{aust} , whereas some residues of the 020_{mart} are still visible (*Fig. 4(b)*), indicating that the amount of martensite decreases in favor of austenite at 425 K. The latter peak disappears completely at 525 K (*Fig. 4(c)*) and only the 110_{aust} peak remains, pointing out that the complete reverse transformation has already taken place. When cooling, the 020_{mart} peak is the first one from the

martensite to appear (Fig. 4(d)). The situation after returning to RT (Fig. 4(e)) shows that the 002_{mart} and $\bar{1}11_{\text{mart}}$ peaks have appeared instead of the 110_{aust} , coming back to the initial situation. The resolution of the position sensitive detector and the short time used for the measurements in order to avoid any degradation of the structure do not allow to better resolve the mentioned peaks. However, this experiment has confirmed that the two separated DSC peaks (Fig. 1(b)) are not due to the transformation to two different martensitic structures, but to the presence of zones with different transformation temperatures transforming to the same martensitic phase (monoclinic B19'). On the other hand, it has been noticed that the decrease of the height of the 002_{mart} and 020_{mart} peaks when heating is not simultaneous but takes place at different temperatures. This may be attributed to a different texture between the regions transforming at different temperatures. Although additional experiments should be necessary to figure out the cause of this inhomogeneity, it is not surprising to find some kind of texture in the crystalline phases of as cast (partially) crystalline melt-spun ribbons, as it has been already reported in Santamarta *et al.*²¹⁾

3.3 Transmission electron microscopy

Transmission electron microscopy (TEM) observations have been performed to as-cast, partially and completely crystallized samples in order to analyze the microstructural evolution during the crystallization process as well as to establish the correlation with previous thermal and structural results.

The observations carried out on as cast specimens reveal the presence of large completely amorphous areas, which supports DSC and XRD results from previous sections. In addition to these amorphous regions, large crystalline zones with big grains (several μm in size) are also present. Although the observation of one or the other of these microstructures depends mainly on the sample that is observed in the microscope, both have been frequently found to coexist together in adjacent zones of the same region as well (Fig. 5(a)), revealing a spherical shape of the big crystalline regions, which form smooth interfaces with the surrounding amorphous material. These big crystalline zones usually show large platelets of martensite corresponding to different variants, in which a high density of dislocations with small precipitates is often distinguished (Fig. 5(b)). Nevertheless, the presence of these defects seems not to hinder the growth of big martensitic variants. All selected-area electron diffraction patterns (SAEDP) from these big platelets have been successfully indexed as monoclinic martensite (B19'). Occasionally, small crystals embedded in the amorphous matrix have also been observed. The regions with small crystals exhibit different distributions, ranging from densely concentrated with relative larger sizes (Fig. 6(a)) to areas with lower concentration and size (Fig. 6(b)). The shape of the small crystals is spherical in regions with lower density and size (Fig. 6(b)), whereas this sphericity is lost in zones with almost no amorphous phase and crystals contacting each other (Fig. 6(a)). The diameters of the small crystals are normally below $0.4\mu\text{m}$ (or even $0.1\mu\text{m}$ in some regions) and their SAEDP show that they are mainly in austenite (inset in

Fig. 5 (a) TEM micrograph of the $\text{Ni}_{50}\text{Ti}_{32}\text{Hf}_{18}$ ribbon in the as cast state showing the interface between an amorphous zone and a crystalline region consisting of 2 big crystals. (b) Detail of a big crystal showing the substructure of the martensite plates.

Fig. 6(a)). However, some of these regions with crystal sizes slightly larger than $0.4\mu\text{m}$ exhibit martensitic structures in SAEDP as well as the typical contrast of self-accommodated plates within the small crystals in bright field images. In addition, no changes on the chemical composition between regions with different microstructures have been observed by EDX measurements, therefore, the crystallization into various microstructures is not promoted by any composition partition.

TEM observations performed after any of the crystallization treatments over T_C described in the section devoted to DSC results confirm the complete crystallization of the previously existing amorphous areas. Figure 7(a) shows a preexisting big crystalline area (similar to that of Fig. 5(a)) surrounded by the new crystallites formed. An enlargement of these crystallites reveals that they have sizes usually below

Fig. 6 Micrographs from the as cast $\text{Ni}_{50}\text{Ti}_{32}\text{Hf}_{18}$ ribbon showing a dense region of small crystallites in austenite (a) with its corresponding diffraction (inset in a) and a region with less and smaller spherical crystals also in austenite (b).

Fig. 7 TEM micrographs of $\text{Ni}_{50}\text{Ti}_{32}\text{Hf}_{18}$ melt spun ribbon crystallized in the DSC with a fast run up to 875 K: (a) shows an interface between a pre-existent big martensitic area with the newly formed crystallites; (b) is a detail of the zone with small crystallites in martensite and its corresponding SADP.

0.2 μm and are mainly filled by different martensite plates (Fig. 7(b)). SAEDP from such areas confirm the monoclinic structure of the martensite, whereas EDX measurements show similar composition. The microstructure of samples after any of those crystallization processes is indistinguishable from each other.

Samples after 1 minute at 775 K still exhibit large amorphous areas, since the ribbon has not been completely crystallized. After this short treatment, the small crystallites embedded in the amorphous regions do not show sharp and perfect spherical shapes as in the as cast samples (Fig. 8), which could be an indication of a not completely isotropic growth as in the $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$.⁹⁾ Further aging at the same temperature promotes the full crystallization of the $\text{Ni}_{50}\text{Ti}_{32}\text{Hf}_{18}$ melt spun ribbon. In fact, the microstructure after 10 min at 775 K is indistinguishable from that obtained

after crystallization over T_C (Fig. 7), as the absence of important differences between their DSC runs already suggested (Figs. 1 and 2). Thus, attending to the present TEM and DSC results, it can be concluded that aging slightly under T_C during enough time produces similar results to the crystallization over T_C . The independence of the microstructure on the annealing temperature, under isothermal treatments above T_C , was also reported in Shi *et al.*⁴⁾ for a $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$ alloy. Additionally, the dense polycrystalline regions containing such a high amount of small grains (Fig. 7) may be only obtained if a high density of crystal nucleation points exists, with almost no place for growing. This means that the energetic cost for the nucleation of new crystals from the amorphous phase in this alloy is rather similar to the growth energy, which promotes a massive crystal nucleation

Fig. 8 Bright field micrograph of the $\text{Ni}_{50}\text{Ti}_{32}\text{Hf}_{18}$ ribbon annealed during 1 minute at 775 K.

Fig. 9 Micrograph of a big crystalline region in the $\text{Ni}_{50}\text{Ti}_{32}\text{Hf}_{18}$ ribbon after 100 minutes at 775 K.

almost independently of the temperature of the thermal treatment, contrary to the case of $\text{Ti}_{50}\text{Ni}_{25}\text{Cu}_{25}$.^{7,9)}

Increasing the aging time at 775 K up to 100 minutes causes a slight growth of the precipitates in the big crystals, which was not detected in previous stages (Fig. 9). In addition, some precipitates could be also present in the small martensitic crystallites, although the complexity of the microstructure does not allow to completely assure this point. Therefore, the calorimetric changes observed here in the last stages of the treatment at 775 K are likely dominated by the rapid nucleation and growth of precipitates, as it has been already reported in the case of as cast fully crystalline $\text{Ni}_{50}\text{Ti}_{32}\text{Hf}_{18}$ ribbons annealed at 775 K.¹⁹⁾ In that work, the precipitation process promoted an important decrease of the

enthalpy change as well as some shift of the transformation temperatures, as the precipitates do not undergo the martensitic transformation and change the chemical composition of the matrix. The $\text{Ni}_{50}\text{Ti}_{32}\text{Hf}_{18}$ alloy is unstable under thermal treatments in austenite at temperatures above 500 K, and fast changes are produced when higher diffusion is allowed by increasing the temperature.¹⁹⁾ These results may also be valid for the present $\text{Ni}_{50}\text{Ti}_{32}\text{Hf}_{18}$ alloy annealed during 100 minutes at 775 K, since the ribbon is already completely crystalline after 10 minutes at 775 K. Thus, any additional aging is somewhat similar to age an initially crystalline sample, and an analogous behavior is expected.

Finally, some *in-situ* experiments have been performed in fully crystallized samples in order to detect differences in the martensitic transformation between the distinct crystalline regions. Increasing the temperature of the specimens in the microscope with a heating holder produces the fully reverse martensitic transformation of the sample. However, a big difference in transformation temperatures between the small and large crystals has been observed: the small crystallites undergo the reverse transformation relatively close to RT, whereas the large crystals require considerably higher temperatures. In a similar way, small crystals transform under cooling at much lower temperatures than the larger crystals. These experiments verify the previous thermal results from the fully crystallized ribbons and illustrate that the calorimetric peak at lower temperatures corresponds to the martensitic transformation of the small crystals, whereas the peak at higher temperatures is associated with the transformation of the as cast larger crystals.

4. Discussion

The existence of large amorphous regions in the studied as cast $\text{Ni}_{50}\text{Ti}_{32}\text{Hf}_{18}$ melt spun ribbon has been confirmed by several techniques. The solidification rate during casting by melt-spinning (values around 10^5 – 10^6 K/s) is high enough to promote a partial amorphization in these alloys during the fast solidification. However, the conditions during the fast solidification are not homogeneous, since a higher solidification rate is expected to occur in the wheel side as a result of a higher heat transfer to the wheel. This fact finally promotes more amorphous regions in the wheel side with respect to the free side, as it has been observed in the present work by means of X-ray diffraction. In addition to this, the origin of a lower martensite/austenite ratio at the wheel side with respect to the free side is also related to the higher solidification rate at the wheel side during the fast solidification. The higher solidification rate during the melt spinning promotes a reduction of the grain size, and thus a decrease in the transformation temperatures, as it has been already shown for Cu-based melt spun ribbons.¹⁾

In order to evaluate the thickness of each side of the ribbon that gives significant contributions to the X-ray spectra shown in this work, the intensity of the X-ray beam as a function of the depth from the surface of the ribbon has been estimated. For this purpose the following expression for the decay of the X-ray intensity inward a pure element, deduced under the kinematical approximation, has been used:^{22,23)}

$$\frac{I(t)}{I_0} = e^{-2\mu t / \sin \theta} \quad (1)$$

where I_0 is the intensity of X-rays on the surface, $I(t)$ its intensity at a thickness t (*i.e.* distance to the incidence surface), μ the absorption coefficient of the element and θ the incidence angle of the beam. Considering that each element contributes with different weights to the absorption of the X-rays, the “average” absorption coefficient for the alloy may be approximated to:

$$\frac{\mu}{\rho} = \sum_i c_i \left(\frac{\mu}{\rho} \right)_i \quad (2)$$

where c_i are the weight concentration for each element.^{22,23)}

Equations (1) and (2) have been applied to the Ni₅₀Ti₃₂Hf₁₈ alloy, considering only the more intense peaks of the experimental diffraction patterns ($2\theta < 70^\circ$). Under these conditions, eq. (1) shows that the intensity of the X-rays beyond 5 μm from the incidence surface is lower than $0.1I_0$. Therefore, the spectra obtained in this work correspond mainly to the first 5 μm from the surfaces of the ribbon. This fact confirms the accumulation of amorphous phase on the wheel side even though some crystalline fraction exists as well (Fig. 3). However, the mixture of amorphous and crystalline phases observed within the same TEM specimens shows that the present situation is different to the one observed in optical micrographs of cross sections in a Ti₅₀Ni₂₅Cu₂₅ as cast ribbon,¹²⁾ in which the wheel side (completely amorphous) was clearly separated from the free side (completely crystalline) by a well defined interface parallel to the faces of the as cast melt-spun ribbons.

As far as the crystallization experiments concern, they clearly promote the splitting of the martensitic transformation in two separated stages, independently of using crystallization temperatures either above or below T_C . The additional calorimetric peak at lower temperatures is related to the transformation of the new crystalline regions formed during the crystallization, which exhibit a very different microstructure with respect to the crystals that already existed in the as cast alloy. Most of these crystals would be located near the wheel side after the crystallization treatments, where a higher density of amorphous phase was present in the as-cast ribbon. The much lower grain size of these regions promotes an important decrease in the transformation temperatures in comparison to the pre-existing big crystals. As it was mentioned before, the decrease of the transformation temperatures when reducing the grain size has been already reported in several SMA, although some discrepancies still exist expressing this dependence in a mathematical way. In addition to this difference, the small crystals in this alloy also show a higher hysteresis than the big crystalline regions. Thermodynamically speaking, the differences in the hysteresis and transformation temperatures are associated with changes in the energy balance equation of the martensitic transformation. A decrease of the transformation temperatures for the new small crystals would imply some rising of the elastic term (*e.g.* due to higher difficulties in the accommodation of the martensitic variants). On the other hand, a larger hysteresis is related with higher frictional terms, indicating that the same martensite exhibits

more difficulties to retransform. Moreover, the term corresponding to the surface energy, which is usually not considered because the volume of the martensitic platelets are generally much bigger than their surface, may play an important role in the case of these small crystals created during the crystallization.

The frequency at which different microstructures are observed by TEM in equivalent samples depends on the depth the observation zone has with respect to the sample surface. This depth is, obviously, very difficult to control during the electropolishing process. In addition, as already mentioned, there is no a sharp division of the different microstructures into layers along the thickness of the ribbon, but a mixture of them whose density depends on the position along the thickness of the ribbon. However, the extensive TEM and XRD studies allowed to identify the different microstructures appearing along the whole thickness of ribbons. In as cast Ni₅₀Ti₃₂Hf₁₈ samples, the big crystalline regions surrounded by amorphous areas forming smooth interfaces (looking as if they were part of spherical crystals) are similar to the ones reported in Ti₅₀Ni₂₅Cu₂₅, where some controversy has been generated around this topic. In Rösner *et al.*⁷⁾ and Santamarta and Schryvers⁹⁾ the spherical shape and smooth interfaces of the crystals have been related to an isotropic nucleation/growth of the crystals by thermal treatments performed after casting the ribbon. However, spherical crystals with diameters up to 10 μm ⁸⁾ or 22 μm ⁶⁾ are also observed in the initial state in the Ti₅₀Ni₂₅Cu₂₅ alloy. The spherical shape and the smoothness of the interfaces in these works were attributed to the fact that the spherical grains were produced somehow during the fast solidification.⁶⁾ In the present work, spherical crystals with smooth interfaces have been already observed in as cast state, thus being evident that they were also produced during the fast solidification. Furthermore, the production of new grains by thermal treatments (or the growth of the existing ones) in Ni₅₀Ti₃₂Hf₁₈ samples do not lead to crystals with so perfect spherical shape and sharp interfaces with the amorphous regions but with local wavy interfaces (Fig. 8), contrary to what was observed in Ti₅₀Ni₂₅Cu₂₅ ribbons.^{7,9)}

Concerning the presence of crystals either in the martensitic or austenitic phase at RT in the as-spun state, the variation in the structure is mainly a consequence of the difference in the grain size (*i.e.* difference in the transformation temperatures). Thus, crystals with grain diameters higher than about 0.4 μm are observed at RT in martensite, whereas the smaller ones are in austenite. On the other hand, the presence at RT of martensitic crystals with diameters below 0.2 μm in fully crystallized samples shows that another factor should play an important role in the transformation temperatures of the small crystals. The spherical crystallites forming smooth “defect-free” interfaces with the amorphous regions in the as-received state likely do not have places in which the nucleation of the martensite is promoted. Therefore, despite of their bigger size, they have lower transformation temperatures than the small crystallites produced by means of subsequent thermal treatments. These crystals have a very high fraction of grain boundaries and also some decomposition of the material could have been produced during the thermal treatment at high temperatures,¹⁹⁾ which

may easily promote the formation of nucleation points for the martensite that help to increase the transformation temperatures. Alternatively, a higher surface energy for the crystalline-amorphous interfaces could be enough for decreasing the transformation temperatures, as reported in Santamarta and Schryvers.²⁴⁾

5. Conclusions

A partially amorphous $\text{Ni}_{50}\text{Ti}_{32}\text{Hf}_{18}$ melt spun ribbon has been characterized by means of DSC, XRD and TEM, putting special efforts on the evolution of the microstructure and the martensitic transformation upon different crystallization treatments. The results obtained in this work show that:

(1) The as-cast $\text{Ni}_{50}\text{Ti}_{32}\text{Hf}_{18}$ exhibits a mixture of amorphous and crystalline phases. The amorphous regions, as well as the crystallites of smaller size, are mostly concentrated in the wheel side as a result of a higher solidification rate during casting, compared to the free side.

(2) As a consequence of this inhomogeneity, a rich variety of microstructures is observed by TEM in the as cast ribbon, depending on the depth of the observation zone formed during electropolishing. The microstructures of as cast ribbons at RT range from completely amorphous regions up to big crystalline zones in martensitic state, which show spherical shapes and smooth surfaces independently of the size of the crystal. On the other hand, the growth of crystals from the amorphous areas by subsequent crystallization treatments leads to crystals with wavy crystalline-amorphous interfaces and thus non-perfect spherical shapes.

(3) A controlled crystallization can be carried out by thermal treatments slightly under T_C , although the microstructure and the calorimetric behavior of the fully crystalline sample do not change notably with respect to the samples fully crystallized over T_C . Irrespective of the crystallization treatment, the microstructure at RT consists of regions with small crystallites ($\sim 0.2\ \mu\text{m}$), mainly in martensite, produced during the thermal treatment (which shows that the energy of nucleation of the crystalline phase is rather low for this alloy), together with the large crystals originated during casting.

(4) The new crystallized regions with small grain size show lower transformation temperatures and higher hysteresis in comparison to the big crystalline zones already existing before crystallization, being another example for the dependence of the transformation temperatures on the grain size, and leading to a two-step transformation as seen in DSC runs. However, the big number of grain boundaries inherent to the new crystallized regions, together with other defects that are probably created during the crystallization treatment, likely play a role in the sense of facilitating the nucleation of martensite, since bigger spherical crystallites having smooth interfaces with the amorphous matrix of the as-cast ribbons have lower transformation temperatures.

Acknowledgements

Financial support to R. Santamarta by means of a grant of the Universitat de les Illes Balears (UIB) is acknowledged. Partial financial support from DGI (HF1999-0056, MAT2000-0862-C03-02 and MAT2002-00319 projects) are also acknowledged.

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