Journal of Non-Crystalline Solids 117/118 (1990) 789–792
North-Holland

QUASICRYSTALS AND AMORPHOUS ALLOYS IN TI-ZR-NI SYSTEM: GLASSFORMING ABILITY, STRUCTURE AND PROPERTIES

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The structure and properties of equilibrium and rapidly quenched Ti-Zr-Ni alloys within Ti-Ti_2Ni-Zr_2Ni-Zr rigion have been investigated. Rapidly quenched ribbons with different thickness have been prepared by melt-spinning technique, which enables to stop the weel quickly during the spinning process. The glass forming ability have been estimated from amorphous ribbon thickness critical values. The quasicrystalline formation range in the rapidly solidified Ti-Zr-Ni alloys and their thermal stability have been determined. It's found that the quasicrystalline phase is formed during melt quenching within the narrow cooling rate range the latter depending upon alloy composition.

1. INTRODUCTION

The discovery of icosahedral and other quasicrystalline phases in the Al-Mn system[1,2] resulted in similar investigations for many alloy systems. By now, quasicrystalline phases have been identifed in a number of alloys (including$(Ti_{1-x}V_x)_2Ni$, x=0,0-0,3 and $Ti_{0.8-x}Zr_xNi_{0.2}$,x=0,2-0,6)[3,4] most of which have a Frank-Casper phase in equlibrium state. Analysis of phase diagrams has shown that many rapidly quenched quasicrystalline phases exist near eutectics formed by an interaction between Frank-Casper phases with a disordered bcc or fcc solid solution. On the basis of this premise we selected for study the Ti-Ti_2Ni-Zr_2Ni-Zr system, the Ti_2Ni-Zr_2Ni section have been investigated earlier[5,6]. This section is of eutectic type formed by the interaction between the intermetallic compounds: Ti_2Ni, the Laves ternary phase ZrTiNi (the $MgZn_2$ type), and Zr_2Ni (the $CuAl_2$ type).

The purpose of this investigation was to define the conditions and the formation range of amorphous and quasicrystalline phases in rapidly quenched alloys of the Ti-Ti_2Ni-Zr_2Ni-Zr system and to determine their binding with the phase diagram.

2. EXPERIMENTAL PROCEDURES

The Ti-Zr-Ni system alloys were prepared from iodide Ti and Zr (99,98%) and electrolytic Ni (99,99%) in an arc furnace in an atmosphere of purified argon. The rapidly quenched ribbons of the alloys have been prepared using a melt-spinning apparatus, which enables to stop the weel within a short time period of 1-2 s and to produce a long ribbon with a continous variation in thickness in the range of about 20-500 μm within one spinning operation. Fig. 1 shows the scheme of the phase composition variation vs. thickness of rapidly quenched ribbon.

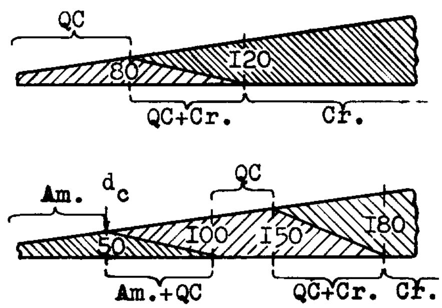

FIGURE 1
The scheme of the phase composition variation vs. thickness of rapidly quenched ribbon (QC, quasicrystalline; Am, amorphous; Cr, crystalline)

The glass forming ability (GFA) of these alloys was estimated by means of the critical thickness, d_C (μm), of amorphous ribbons[7]. An X-ray diffraction

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analysis was carried out on powders in Cu K_α radiation. The diffraction lines were indexed in the system of icosahedral indices by Bancel techique[8]. Differential scanning calorimetry (DSC) was performed using a Perkin Elmer DSC-2. The transitions between the metastable state of rapidly quenched alloys and their equilibrium states were determined by means of DSC experiments. The solidus and liquidus temperatures of the alloys were registered by the DTA technique in the purified helium atmosphere at a heating/cooling rate of 15 K/min. The specific resistivity was measured using a standard four-point technique.

3. RESULTS AND DISCUSSION

The construction of the liquidus surface of the phase diagram for the Ti-Ti_2Ni-Zr_2Ni-Zr system presented in Fig. 2 is based on DTA and X-ray analysis. Interactions between intermetallic compounds Ti_2 Ni, Zr_2 Ni, ZrTiNi and bcc(Ti,Zr) solid solution result in formation of two low-temperature eutectics E_1 (1185 K) and E_2 (1175 K). One should note that the crystallization region of the Laves ternary phase ZrTiNi is rather large.

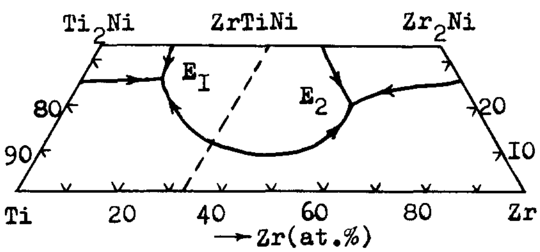

FIGURE 2
Liquidus surface of the Ti-Ti_2Ni-Zr_2Ni-Zr system

X-ray analysis of the rapidly quenched ribbons with variation in thickness has shown that 100% quasicrystalline phase is formed for several alloys in the definite thickness interval (i.e. within the narrow range of cooling rates).

For certain alloy compositions increasing of the cooling rate results in amorphous phase formation. GFA of the Ti-Ti_2Ni-Zr_2Ni-Zr system alloys estimated in terms of critical thickness is presented on Fig. 3.

The highest GFA (d_c =680 μm) has been found for the alloys lying near the binary eutectic formed by interaction of glass forming phases ZrTiNi and Zr_2Ni (Fig. 3). We have discussed the similar GFA increasing in the vicinity of binary zirconium eutectic earlier[6] .

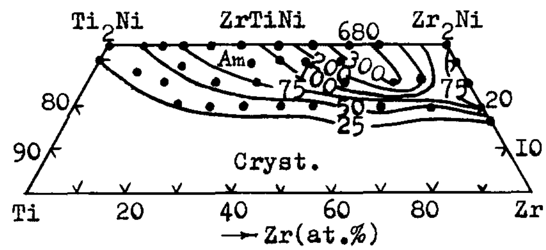

FIGURE 3
Critical thickness, d_c (μm), of amorphous ribbons of Ti-Ti_2Ni-Zr_2Ni-Zr alloys

We have observed the GFA decrising for alloys within the range of ternary zirconium eutectic E_2 formed by interaction between ZrTiNi and Zr_2Ni glass forming phases with bcc (Ti,Zr) solid solution, in comparision with the alloys lying in the vicinity of binary zirconium eutectic.

The formation range of the quasicrystalline phase during melt quenching is shown in Fig. 4. According to Fig. 4 the quasicrystals are formed in a wide concentraition range of the system.

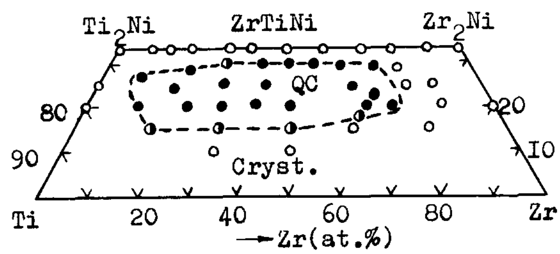

FIGURE 4
Compositional range for the formation of quasicrystalline phases in rapidly solidified Ti-Ti_2Ni-Zr_2Ni-Zr alloys:● -quasicrystalline;◐ -quasicrystalline plus crystalline; o -crystalline

It seems that quasicrystalline phase formation in this system is due to the interaction between

Laves phase ZrTiNi and bcc (Ti,Zr) solid solution. It should be noted that icosahedral coordination shells dominate in the structure of the Laves phase ZrTiNi. The wide concentration interval of the quasicrystalline phase formation is associated with a wide range of Laves phase existence.

For example the X-ray diffraction pattern of quasicrystalline $Ti_{53}Zr_{27}Ni_{20}$ alloy is shown in Fig. 5. The diffraction peak at 2.601 $Å^{-1}$ is identified as the (100000). Although this choice is convenient, it gives a quasicrystalline lattice constant α_R[9,10] of 1.202 Å, which is too small for an atomic distance. A more likely choice of the dimension of the rhombohedra which may be used in the quasicrystalline tilling[10,11] (where τ is the golden mean, $(1+\sqrt{5})/2$).

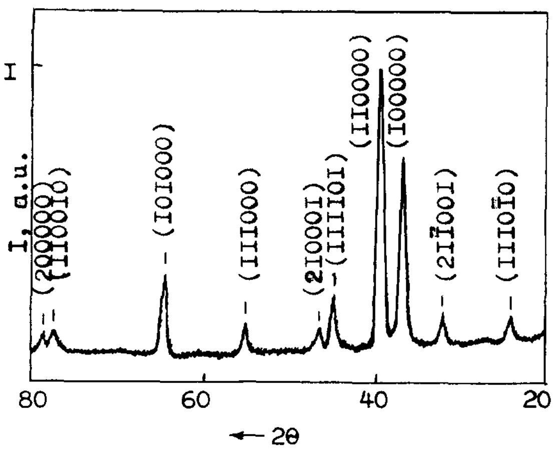

FIGURE 5
X-ray powder diffraction pattern (CuK_α) of quasicrystalline $Ti_{53}Zr_{27}Ni_{20}$ alloy

It was established by DSC that the quasicrystalline phase in $Ti_{53}Zr_{27}Ni_{20}$ alloy retains its stability up to 960 K (Fig. 6a). The recrystallization process was inferred from an endothermal effect which is equal in intensity to the head of the polymorphic transition. The activation energy calculated for the phase transition is E_a =5.5 eV/atom. The crystallization and recrystallization stages during the heating of rapidly quenched alloys are usually accompanied by exothermic effects. This type of transition of the quasicrystalline phase is the evidence of its metastability.

The decay of the quasicrystalline phase occurs completely only after three heating-cooling cycles over the range 300-1000 K. Each successive heating leads to a decrease in the effects of the DSC curve and to a lowering of the phase transition temperature by 20-50 K.

It was established by X-ray analysis that in the rapidly quenched $Ti_{53}Zr_{27}Ni_{20}$ alloy heated up to 960 K and cooled to 300 K the structure of the quasicrystalline phase is conserved completely. The relative thermal stability of quasicrystalline phase is rather high, amounting to 0.87 of melting point T_m =1113 K.

The specific resistivity of the quasicrystalline phase is ρ_{300} =185 $\mu\Omega$ cm. The value is close to the values of ρ which we found previosly for amorphous

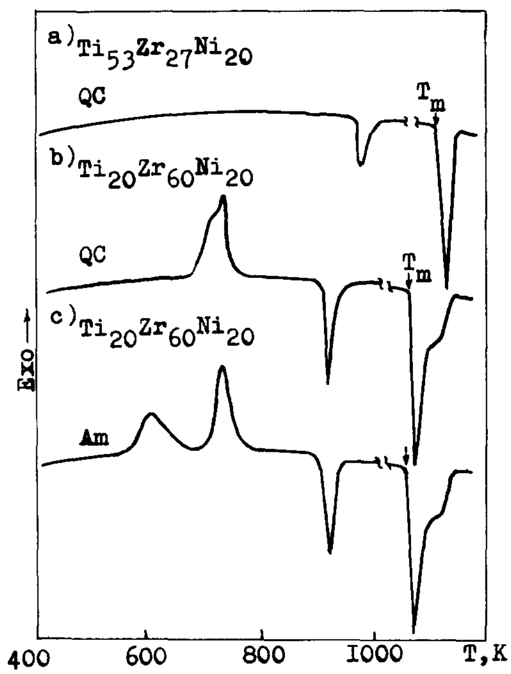

FIGURE 6
DSC and DTA (effects of melting) curves of quasicrystalline $Ti_{53}Zr_{27}Ni_{20}$ (a) and $Ti_{20}Zr_{60}Ni_{20}$ (b) and amorphous $Ti_{20}Zr_{60}Ni_{20}$(c) alloys (heating rate, 15 K/min): QC, quasicrystalline; Am, amorphous

alloys of this system. The microhardness of the quasicrystalline phase is HV=7300 MPa.

It may be supposed from composition of glass and quasicrystals forming ranges that there's a possibility of quasicrystals formation from the melt as well as during amorphous structure heating.

In Fig. 6b,c DSC and DTA curves for rapidly quenched $Ti_{20}Zr_{60}Ni_{20}$ alloy prepared in quasicrystalline and amorphous states as a result of different cooling rates are shown.

The highest exothermal maximum on the DSC curve is associated with the ZrTiNi-phase formation and the endothermal one - with the metastable quasicrystalline phase decomposition. It's clear from Fig. 6b,c that DSC curves of $Ti_{20}Zr_{60}Ni_{20}$ alloy in these two states differd by the low temperature exothermic reaction observed for amorphous state. However an X-ray analysis of the alloy showed only amorphous phase existence after this low-temperature transformation. It's possible that only very fine quasicrystals (less than 5 nm) form during low-temperature transformation mentioned above. HTEM investigation is necessary to resolve this problem.

Thus it should be concluded that:

1. Quasicrystals in Ti-Ti_2Ni-Zr_2Ni-Zr system form within narrow cooling rate range, which makes difficult their preparation and investigation.
2. Comparison of the phase diagram and quasicrystals formation range for the system investigated allows to suppose that quasicrystals don't posses any specific stoichiometry and their formation results from Laves phase and bcc (Ti,Zr) based solid solution interaction.
3. Quasicrystalline phase is metastable within this system and exists up to high temperatures.

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