Reversible Amorphization in Laser-Quenched Titanium Alloys

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Metastable crystalline and amorphous phases were obtained by pulsed-laser quenching of thin Au-Ti and Cr-Ti films. Subsequent furnace annealing was found to convert metastable crystalline modifications into amorphous ones for certain compositions in both systems. In $Cr_{1-x}Ti_x$ ($x \sim 0.7$), a further annealing step at a higher temperature leads back to the initial metastable crystalline phase, thus making possible repeated crystalline to amorphous to crystalline transitions by simple thermal cycling. This phenomenon is unrelated to fast diffusion, but can be explained on the basis of free-energy considerations.

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Irradiation of thin films on suitable substrates by short laser pulses is a proven method to achieve melt quenching at very large cooling rates.¹ As a result, glass formation is observed in binary metallic systems over extended ranges of composition. Certain melts, however, resist glass formation even by laser quenching, but form metastable crystalline phases instead. Laser-quenched glassy films on Au-Ti and Cr-Ti have been described previously.² In the present Letter we describe laser-quenched crystalline phases of Au-Ti and Cr-Ti with the intriguing property of turning amorphous upon subsequent furnace annealing.

The metallic films were electron-gun-deposited multilayers, 150 nm thick, on substrates of either sapphire or tungsten. By irradiation with 50-ns full width at half maximum ruby-laser pulses the films were melted, homogenized, and subsequently quenched. Numerically calculated cooling rates with these parameters are 1×10^9 K/s for films on sapphire and 3×10^9 K/s for films on tungsten substrates.¹ After quenching, as well as after subsequent annealing in a high-vacuum furnace (10^{-6} mbar or better), the films were investigated by x-ray diffractometry and electrical resistivity measurements. The absence of lines and the presence of a halo in the x-ray spectrum, together with an increased resistance, was taken as evidence of amorphousness in the present work.

With reference to the Au-Ti system, glasses were obtained on tungsten substrates near the compositions $Au_{70}Ti_{30}$, $Au_{60}Ti_{40}$, and $Au_{40}Ti_{60}$. On sapphire substrates the first composition gave the equilibrium structure (Au_4Ti and Au_2Ti compounds), while the last gave a glass. The middle composition yielded equilibrium compounds, but not those predicted by the phase diagram³ ($Au_4Ti + AuTi_3$ instead of $Au_2Ti + AuTi$). We refer to this structure as metastable crystalline (c_m). Upon furnace annealing at slowly rising temperature, all glassy Au-Ti films crystallized near 400 °C into their equilibrium configuration (c_e), as reported earlier.² The metastable crystalline films $Au_{60}Ti_{40}$, on the other hand, turned amorphous near 350 °C, before eventually assuming the equilibrium configuration near 400 °C. Figure 1 shows their resistivity monitored during isothermal annealing at 350 and 400 °C: The two transitions, metastable crystal to amorphous $(c_m \rightarrow a)$ and amorphous to equilibrium crystal $(a \rightarrow c_e)$, are clearly manifested, the first by an increase and the second by a decrease in the resistivity. The two transitions were verified by xray diffraction: The $c_m \rightarrow a$ transition resulted in the buildup of a characteristic halo while the line spectrum gradually faded away. After crystallization, every line present could be identified with an equilibrium compound (oxide lines were detectable only after annealing above 900 °C). Besides, the difference between the resistivities of the c_m and c_e films is probably unrelated to the phases present, but just reflects the fact that c_m represents a rapidly quenched and c_e an annealed film.

In the *Cr-Ti* system glasses are obtained on sapphire substrates between 45 and 60 at.% Ti.² The use of W extends the glass-forming range from 45 to at least 90 at.%. Crystallization temperatures for glasses of all compositions are near 650 °C. As-quenched films on sapphire with compositions above 60 at.% contained the bcc solid solution (β phase) that is stable at high



FIG. 1. Evolution of the resistivity of an Au₆₀Ti₄₀ film during isothermal annealing at 350 and 400 °C. c_m , meta-stable crystalline; a, amorphous; c_e , equilibrium crystalline.

temperatures, but metastable between room temperature and at least 670 °C.³ As-quenched films were annealed isothermally at 600 and 800 °C (usually for 30 min) and then analyzed at room temperature. The results—slightly simplified—are schematized in Fig. 2(a). Films with the metastable β phase turned amorphous upon annealing at 600 °C. Subjected to a second annealing step at 800 °C, the freshly amorphous films crystallized, either—depending on composition and



FIG. 2. (a) Schematic of annealing results of Cr-Ti films. The β phase (bcc solid solution) is metastable at room temperature. Open circles and open squares indicate the structures of as-irradiated films on tungsten and sapphire substrates, respectively. The behavior on a sapphire substrate (dashed arrow), shown only at 60 at.% Ti, is the same for all three compositions. (b) Relevant section of diffractometer traces illustrating the reversible $a \rightarrow \beta \rightarrow a$ transition in Cr₃₀Ti₇₀ films. The diffraction line at 20° is from the W substrate.

substrate material-forming the equilibrium configuration c_e (Cr₂Ti + α -Ti) or returning to the β phase. Films with 70 at.% Ti on W could be switched back and forth between the β and amorphous phases by application of alternating annealing steps at 600 and 800 °C. Figure 2(b) shows sections of diffractometer traces taken from the same film after irradiation (curve az), after annealing to 800 °C (curve β), and after annealing to $600 \,^{\circ}$ C (curve a). The line at $\theta = 20^{\circ}$ belongs to the W substrate, whereas that at 20.6° is the (110) line of the β phase.⁴ The $\beta \rightarrow a$ transition is evidenced by the disappearance of all sharp diffraction lines, and the concomitant appearance of the characteristic halo at 21.3°. Transitions $\beta \rightarrow a$ were also seen on sapphire substrates, but the amorphous phase formed was somewhat different from that on W and did not show the reversible amorphization feature.

The occurrence of these unusual phase transitions during furnace annealing suggests that thermodynamic, in addition to kinetic, constraints are responsible for them. In Fig. 3 we show a Gibbs free-energy diagram for the Au-Ti system, with curves for the four equilibrium compounds as well as for the amorphous phase at a temperature of 400 °C (similar curves result at 350 °C). The heats of formation used in the calculation were estimated by Miedema's method.⁵ The amorphous phase was simply treated as an undercooled normal liquid (regular solution model). Consider a mixture with 40 at.% Ti (arrows). It can be seen that at 400 °C (as well as at room temperature) the state present after irradiation (c_m) has a larger free energy than the amorphous phase (a), which in turn has a larger free energy than the equilibrium configuration (c_e) . Hence, both transitions observed $(c_m \rightarrow a \text{ and } a \rightarrow c_e)$ are in accordance with thermo-dynamics. The $a \rightarrow c_e$ transition cannot occur below $T_{ac} \sim 400 \,^{\circ}\text{C}$, but apparently the mixing reaction $(c_m \rightarrow a)$ is possible at a lower temperature (although at a slower rate, see Fig. 1). This effect is analogous to that invoked in a number of solid-state amorphization reactions reported recently.⁶ They all rely on the fact that the apparent activation energy for diffusion (that governs mixing) is considerably smaller than that for crystal nucleation. Systems with this property are known as fast diffusers. Au-Ti can, to some extent, be considered a member of this group.⁷ It must be emphasized, however, that mere furnace annealing of virgin films of Au₆₀Ti₄₀ at temperatures between 200 and 350 °C produces a mixture of compounds rather than an amorphous phase.

What remains to be explained is the structure of the as-irradiated $Au_{60}Ti_{40}$ film. The presence of the two "outer" compounds Au_4Ti and $AuTi_3$ in place of the neighboring ones may be related to the fact that we start from a stack of elemental layers. Even though



FIG. 3. Gibbs free-energy diagram of the Au-Ti system at 400 °C. c_m gives the structure after irradiation, c_e the equilibrium configuration for the 40 at.% Ti sample considered. Curve *a* is the free energy of the amorphous phase, treated as an undercooled liquid.

the solidified films are typically found to be homogeneous to within a few atomic percent or better,¹ it may be speculated that homogenization is not fully completed at the time when nucleation starts, giving the "outer" compounds, which require less mixing, kinetic advantages over the "inner" ones.

Whereas the observation with Au-Ti can be explained essentially along the lines of solid-state amorphization of fast diffusers, the case of Cr-Ti is different, since the metastable β crystal has the same composition as the amorphous phase that grows from it: This is, to our knowledge, the first demonstration of diffusionless solid-state amorphization. Moreover, the $\beta \rightarrow a$ transition is reversible in some cases. In a previous publication¹ we have conjectured that the effect could be related to stress. The β phases in asquenched films on sapphire were found to have lattice constants about 1.5% smaller than given in the literature,⁸ independent of the film composition. This amount of deviation is consistent with compressive stress exerted by the substrate on the film, due to the existing mismatch in the thermal expansion coefficients. However, careful experiments have shown that



FIG. 4. Gibbs free-energy diagrams of Cr-Ti at 600 and 800 °C. Arrows indicate the transitions shown in Fig. 2(a). α and β stand, respectively, for α -Ti (hcp) and the bcc solid solution. Cr₂Ti is a Laves phase. The curves for the amorphous phase (curves *a*) are estimates.

stress relaxation *precedes* the $\beta \rightarrow a$ transition (the xray diffraction lines shift to their nominal positions before they disappear). This seems to rule out stress effects. We believe, however, that at least a qualitative explanation can again be given in terms of ordinary thermodynamics.

Free-energy curves at 600 and 800 °C consistent with the results of Fig. 2 are shown in Fig. 4. All curves except those for the amorphous phase (curve a) were calculated from accepted experimental data.⁸ A linear extrapolation of the experimental liquid-phase data gives free energies for the amorphous phase far too large to explain our observations (about +5.5kJ/mol at 800 °C near the equiatomic composition). The curves labeled a in Fig. 4 represent a regularsolution model with an excess-energy parameter chosen to fit our experiment. It can be seen to take the amorphous phase to be far more stable than the extrapolated melt. The curves shown are, on the other hand, consistent with the prediction from Miedema's model⁵ as well as with a recent prediction of enthalpy differences between liquids and glasses by Saunders. On the basis of these curves, amorphization of the β phase at 600 °C can be seen to be allowed for 60 as well as 70 at.% Ti. Moreover, at 800 °C the relative position of the β and a free-energy curves is reversed near 70 at.% and allows the observed $a \rightarrow \beta$ transition. The reason for the reversal of the free-energy curves is that the amorphous phase is taken to have a constant negative heat of mixing, while the β phase is known to have a positive heat of mixing that decreases with temperature.⁸

In summary, we have shown that two kinds of solid-state amorphization reactions can be observed in laser-quenched films. The mechanism involved in Au-Ti is related to the fast-diffuser mechanism proposed previously,⁵ while in the case of Cr-Ti amorphization is diffusionless and due to intrinsic thermodynamic properties of the system. Similar behavior might arise in a number of other binary systems with high-temperature solid solutions.

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