

FIG. 4. Natural log of the ordering time constant (τ) as a function of reciprocal absolute temperature.

value for the activation energy does not agree with the value of 45 kcal/mol extracted from reported resistivity results⁴ on ordering in Pt_1Co_1 , it is reasonably close to an anticipated value based upon ordering by vacancy controlled atomic mobility, since it is only slightly less than the values of 61–66 kcal/mol typically reported^{5,6} for platinum and cobalt self-diffusion activation energies.

The puzzling feature apparent in the magnetization data as presented typically in Fig. 2 is that the results at all ordering temperatures do not extrapolate to the 41.3-emu/g value expected at zero time. The extrapolated value indicates that a 5% decrease in the magnetization occurs as an initial transient after the quench even before the ordering reaction is initiated. Initial transients are frequently encountered in many structural transformations, particularly the amorphous-to-crystalline variety.⁷ It is tempting to suggest that the initial magnetic transient apparent with atomic ordering

in Pt_1Co_1 is associated with nucleation while the subsequent annealing stage characterized by the observant first order response kinetics results from growth in this second order phase transformation phenomena. This simple separation of nucleation and growth mechanisms by magnetic measurements makes the questionable assumption that nucleation will result in a measurable change in the magnetization. An alternate possible explanation for the initial transient behavior also exists. Assuming that the nucleation and growth mechanisms are not separable by magnetic measurements and are both essentially contained in the first order response kinetics, the transient behavior could result from the presence of an intermediate metastable phase that exists when quenching from the completely disordered fcc structure to the completely ordered Pt_1Co_1 structure where the room-temperature saturation magnetization value of this intermediate phase would be 5% less than that of the disordered phase. There is a suggestion⁸ in the literature that such a phase may exist. To distinguish between these two possible explanations, the nature of this particular transient in the Pt_1Co_1 system is now being investigated.

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Thermal stability of thin-film amorphous W-Ru, W-Re, and Ta-Ir alloys

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The crystallization behavior of self-supporting thin-film amorphous W-Ru, W-Re, and Ta-Ir alloys has been studied with transmission electron microscopy. Crystallization temperatures have been observed which are much lower than the temperatures predicted by a semiempirical model: the highest observed temperatures are 775 °C for W-Ru and W-Re alloys, and 900 °C for the Ta-Ir alloys. All three systems show maximum thermal stability at a composition expected using enthalpy considerations.

Buschow and Beekmans proposed a simple kinetic model to predict the thermal stability of binary amorphous alloys.¹ In this model the activation energy for crystallization is taken proportional to the formation enthalpy of a hole (ΔH_h) the size of the smaller type of atoms, and the crystal-

lization temperature is given by $T_c \approx 7.5\Delta H_h$ (T_c in Kelvin, and ΔH_h in kJ/mole). An attractive feature of this approach is that the crystallization temperature of amorphous alloys can be estimated for cases in which experimental data are not yet available in the literature. Amorphous alloys with high

thermal stability are interesting from a fundamental point of view as well as for many applications. The amorphous alloy $Ta_{55}Ir_{45}$ is at present the alloy with the highest reported T_c of 1010 °C (Ref. 2), in good agreement with the semiempirical model which predicts a T_c of approximately 1120 °C. However, even higher T_c 's may be expected for alloys which have large hole formation enthalpies. In order to examine this correlation we have studied the stability of W-Ru and W-Re alloys which, according to the model, should have crystallization temperatures of approximately 1250 and 1480 °C, respectively. For comparison, thin films of amorphous Ta-Ir were also studied.

Thin films of Ta-Ir, W-Ru and W-Re alloys were prepared by codeposition in a base vacuum less than 5×10^{-6} Pa and at a typical deposition rate of 0.5 Å/s. The thin films were deposited onto a NaCl substrate at a temperature less than -100 °C. The thickness of the films was between 300 and 400 Å. After deposition the NaCl substrate was dissolved in water and the films were placed on Cu or Mo transmission electron microscope (TEM) grids. The compositions of the W-Ru alloys were determined using Rutherford backscattering spectrometry (RBS) and the compositions of the W-Re and the Ta-Ir alloys were determined using energy dispersive x-ray spectroscopy (EDS). For each temperature the samples were annealed for 15 min in a vacuum less than 10^{-4} Pa and the crystallization temperatures and structures were determined with TEM.

The results of the W-Ru system are summarized in Fig. 1. The alloy with 15 at. % Ru was crystalline at room temperature and the phase was identified as a solid solution of Ru in bcc W. The alloy with 25 at. % Ru consisted at room temperature of some large crystallites in an amorphous matrix. After storage at room temperature for a few days, the sample was completely crystallized and the structure was a solid solution of Ru in bcc W. The alloy with 35 at. % Ru was amorphous at room temperature and did not crystallize until heating at 775 °C. The structure after crystallization could be identified as a solid solution of W in hexagonal Ru. The alloy with 65 at. % Ru was crystalline at room tempera-

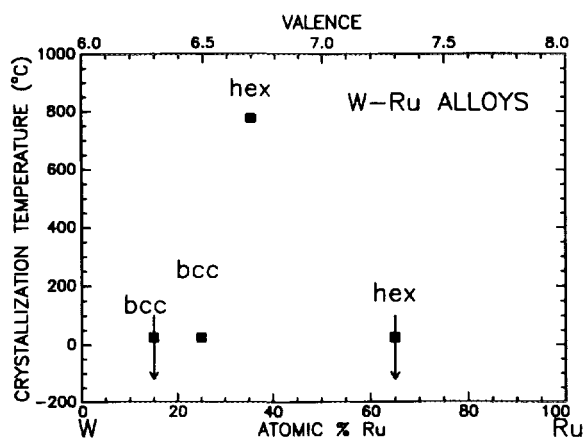


FIG. 1. Crystallization temperatures and structures of the W-Ru alloys. The arrows indicate that this alloy was already crystalline at room temperature and therefore has a crystallization temperature lower than the value plotted. In this system crystallization involves a polymorphic transition. We observe a maximum thermal stability at a valence of approximately 6.6.

ture and consisted of a solid solution of W in hexagonal Re. In each of those alloys, the grain sizes after crystallization were typically between 0.1 and 1 μm which is much larger than the thickness of the films. At all compositions, a single phase structure exists after crystallization and therefore the crystallization process involves a polymorphic transition. The phases present after crystallization are solid solutions in which the atoms do not need to move over large atomic distances for the crystallization process to occur, i.e., no long-range diffusion is needed.

Figure 2 shows the results for the W-Re alloys. The points marked with a filled circle were obtained by Collver and Hammond.³ The alloy with 16 at. % Re was crystalline at room temperature. The diffraction pattern shows that it consists of a solid solution of Re in bcc W. The other alloys were amorphous at room temperature. The alloy with 41 at. % Re crystallized at a temperature of 200 °C into a solid solution of Re in bcc W. The alloys with 51 and 53 at. % Re crystallized at 725 and 775 °C, respectively, and both exhibited the σ -WRe structure. The alloys with 73, 78, and 89 at. % Re crystallized at 650, 600, and 300 °C, respectively. These latter alloys consisted of a solid solution of W in hexagonal Re after crystallization.

The alloy with 16 at. % Re showed an average grain size of 100 Å at room temperature. The other alloys showed grain sizes of typically 0.1–1 μm after crystallization. We observe crystallization into a single phase at all compositions. Therefore, like in the W-Ru system, crystallization in this system involves a polymorphic transition. Wilson observed that ordering in binary σ phases is coupled to the difference in size of the constituent atoms⁴ and since the W and the Re atoms have almost the same radii, very little ordering is expected to be present in the W-Re σ phase. In this σ phase, like in solid solutions, the atoms only need to move over small atomic distances for the alloy to crystallize. Thus, crystallization in the W-Re system also appears to proceed without long-range diffusion.

The plot in Fig. 3 shows the Ta-Ir data. These alloys were all amorphous at room temperature. The alloys with 17 and 27 at. % Ir crystallized at 850 °C. The alloy with 42

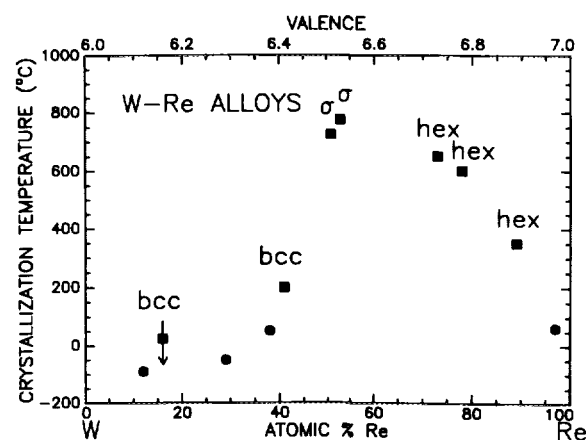


FIG. 2. This plot shows the W-Re crystallization temperatures. The points marked with filled circles were obtained by M. M. Collver and R. H. Hammond (see Ref. 3). Structures after crystallization are indicated above the measurements. Crystallization involves a polymorphic transition in this system. A maximum thermal stability is observed at a valence of 6.6.

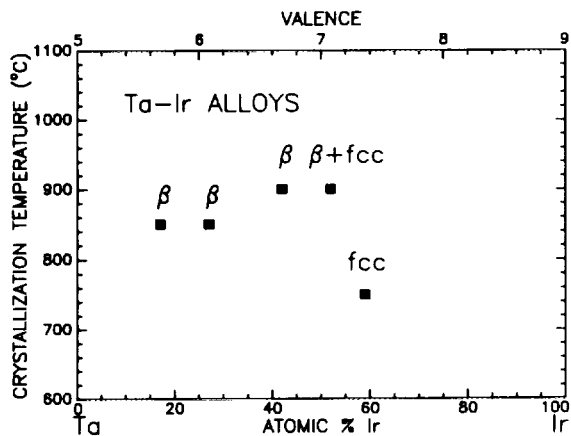


FIG. 3. The Ta-Ir crystallization temperatures. The first-formed crystalline phase is indicated above each point. In this system crystallization involves a phase separation in which at all compositions both the β -Ta and the fcc Ir phases are present at completion of the crystallization. We observe a maximum thermal stability at a valence of approximately 6.9.

at. % Ir crystallized at 900 °C. Crystallization in those three alloys starts by formation of the β -Ta phase (the same phase identified by Nastasi *et al.* in the Cu-Ta system^{5,6}). Crystallization proceeds to completion by formation of both the β -Ta and the fcc Ir phases. The alloy with 52 at. % Ir crystallized at 900 °C. During crystallization both the β -Ta and the fcc Ir phases appear at the same time and after crystallization has been completed both phases are present. The alloy with 59 at. % Ir crystallized at 750 °C. In this alloy crystallization starts by formation of the fcc Ir phase, after which crystallization proceeds by formation of both the β -Ta and the fcc Ir phases. The grain size after crystallization was approximately 200 Å in all the alloys. The phases that are observed after crystallization indicate that the Ta-Ir system crystallizes by phase separation. In order to achieve phase separation the atoms must move over large distances, roughly half the size of the grain. Therefore, long-range diffusion is needed and the crystallization process is different from that in the W-Ru and W-Re systems.

The crystallization temperatures determined in this paper are well below the temperatures predicted by the semiempirical model. In the W-Ru and W-Re systems this low T_c can be explained by the kind of crystallization that is involved: polymorphic transitions without long-range diffusion. In these cases the model of Buschow and Beekmans is not applicable because the basic assumption in this model is that long-range diffusion of the smaller atoms must occur for crystallization to take place.¹ Similar deviations have been observed earlier in studies of the thermal stability of alloys with a positive heat of formation.⁵ These studies show that alloys which crystallize via a polymorphic transition have a much lower T_c than predicted.

In the Ta-Ir system long-range diffusion occurs during crystallization, but the observed crystallization temperatures are still lower than expected. This result might be due to a thin-film effect because Davis *et al.* observed a crystallization temperature of 1010 °C in much thicker samples which is in better agreement with the model.² The thin-film

effect can be explained by the fact that the atoms are more mobile at the surface than in the bulk material and therefore it is easier to nucleate the crystalline phases in the thin films than in bulk materials. The observed T_c is less than the predicted temperature even in the case of phase separation, which indicates that in thin-film amorphous transition metal alloys the Buschow and Beekmans model is not applicable for large hole formation enthalpies. Thus, the model of Buschow and Beekmans should also be modified to account for nucleation effects.

The relatively low crystallization temperature is not the only point that is in disagreement with the semiempirical model. In the W-Ru (Fig. 1) and W-Re (Fig. 2) systems the crystallization temperature exhibits a strong dependence on composition: the crystallization temperature varies over 700 °C for the different compositions. The observed peak in T_c cannot be explained by the simple hole-formation enthalpy model because these enthalpies do not differ very much for different compositions and they increase monotonically over the whole composition range. The Ta-Ir system (Fig. 3) also shows a peak in the crystallization temperature as a function of composition, although less pronounced than in the W-Ru and W-Re systems. These peaks can be explained by the Miedema and Niessen calculations of the structural term in the enthalpy of formation of the fcc, bcc, and hcp structures for the transition metals as a function of valence (the valence is obtained by calculating a weighted average of the valences of the pure constituents).⁷ They show that the difference in enthalpy for the three structures is zero at a valence of 6.7. The driving force for the crystallization process is given by minimizing $\Delta G = \Delta H - T\Delta S$. When ΔH tends to zero the entropy term $T\Delta S$ becomes more important. Because the entropy is larger in the amorphous phase than in the crystalline phase the minimization of ΔG tends to favor the amorphous phase most at a valence of 6.7. Therefore, the amorphous phase is expected to be most stable at this valence.

In the Figs. 1, 2, and 3 the valence is plotted at the top scale. In the W-Ru and W-Re systems the peak in crystallization temperature occurs at a valence of approximately 6.6 and in the Ta-Ir system at approximately 6.9. Those values are in good agreement with the predicted value of 6.7. Also, the observed structures in the W-Ru and W-Re systems are in good agreement with the structures predicted by the Miedema and Niessen calculations: the enthalpy calculations show that for valences smaller than 6.7 the bcc phase is most stable and for valences larger than 6.7 the hcp structure is most stable. In the W-Ru system the observed phase after crystallization for valences of 6.3 and 6.5 is indeed the bcc structure and the observed phase for valences of 6.7 and 7.3 is the hexagonal structure. In the W-Re system we observe the bcc structure after crystallization for valences of 6.2 and 6.4 and the hexagonal structure for valences of 6.7, 6.8, and 6.9. The observed fcc structure in the Ta-Ir system can also be considered to be in agreement with the Miedema and Niessen calculations because this system shows phase separation and therefore the valence in the crystallized alloy will locally differ from the valence in the amorphous alloy. The peaks in the crystallization temperatures are more pro-

nounced in the W-Ru and the W-Re systems than in the Ta-Ir system. Therefore, we may conclude that the structural enthalpy difference is more important when crystallization involves a polymorphic transition than in the case of phase separation. This is not surprising because in the case of phase-separation kinetics it is much more important than in the case of a polymorphic transition and the Miedema and Niessen point only concerns free energy.

The conclusion of this study is that the W-Ru and W-Re alloys show polymorphic crystallization temperatures which are well below the temperatures predicted by the simple semiempirical model. The Ta-Ir crystallization temperatures are also less than predicted, but they may be within the uncertainty limit evident in the theory of Ref. 1. Therefore, the different types of crystallization mechanisms show a different crystallization behavior and thus, the thermal stability of amorphous alloys should be investigated for each crystallization mechanism separately. The Miedema and Niessen enthalpy calculations present us a method to predict the composition of the most stable amorphous alloy.

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Production of the midgap electron trap (EL2) in molecular-beam-epitaxial GaAs by rapid thermal processing

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Rapid thermal processing (RTP) using halogen lamps for molecular-beam-epitaxial (MBE) *n*-GaAs layers was investigated by deep-level transient spectroscopy. RTP was performed at 800 °C for 6 s with a proximity capping method. It was found that the $E_c - 0.82$ eV electron trap (EL2) was produced by RTP. The depth profile of EL2 was flat. The spatial variations of EL2 produced by RTP were observed across the MBE layers. The EL2 concentration increased by about two orders of magnitude toward the edge from the center of the samples ($\sim 18 \times 16$ mm²). It was thought that the spatial distribution of EL2 corresponded to that of thermal stress induced by RTP.

Traps in *n*-GaAs grown by molecular-beam epitaxy (MBE) have been reported by several investigators.¹⁻⁴ Several electron traps have been observed, and the dependence of the trap concentration on the growth conditions has been reported. On the other hand, it is important to study deep levels in high-temperature processed MBE GaAs, since epitaxial layers receive high-temperature processing in device fabrication. To our knowledge, only a few reports about this subject are available at present.^{5,6} Xin *et al.*⁶ have indicated

that the EL2 electron trap is created in MBE GaAs layers by Si₃N₄ capped furnace high-temperature processing.

Recently, rapid thermal processing (RTP) has been used successfully to activate implanted impurities in GaAs and reported to have several advantages over conventional furnace processing.^{7,8} Furthermore, it has been reported that RTP is very suitable for MBE grown GaAs-AlGaAs heterostructure device fabrication due to the low-dopant diffusion.^{9,10} Therefore, there is considerable interest in the study