

CONTROLLED NUCLEATION OF UNDERCOOLED GE-NI MELTS BY CLUSTERS

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Clusters of Si, Ni and Cu produced by sputtering the corresponding targets were introduced into undercooled $\text{Ge}_{74}\text{Ni}_{26}$ melts respectively. As soon as Si clusters were introduced to the melt at an undercooling of 136 or 166 K, nucleation was induced. When triggered by Si, Ni and Cu clusters during continuous cooling of the melt, onset temperature of nucleation was 1009, 975 and 987 K respectively, which are much higher than 904 K, at which nucleation happened without triggering by clusters. The curvature effects on structure evolution of the clusters in the undercooled melt provide an explanation of the present experimental results.

1. Introduction

Undercooling of metal alloys has been the subject of extensive study for many years due to its relevance to the development of metastable microstructures and the revelation to solidification mechanism [1, 2]. In a metallic melt, atoms will approach each other statistically to distances comparable to the atomic spacing in the solid, forming solid-like clusters. With increasing of the undercooling of the melt, the cluster size will also be increased. When clusters reach a critical size, r^* , nucleation happens [3]. Those clusters with the critical size are called nuclei. Up to the early 1950s, it was believed that the short range order of the clusters in the undercooled melts resembles that of the corresponding crystalline phase which nucleates from the melt, because the densities of the melt and the crystal differ only slightly [4]. Accordingly, the structural influences of cluster (with a short-range order) on nucleation remain disregarded. However, recent researches on nucleation [5], undercooling of metallic melts [6], structure of free clusters in mass spectra [7, 8], quasicrystalline phase formation during solidification [9, 10], structure relaxation in amorphous phases [11] etc. have already cast suspicion on the similarity in structures of the clusters and the crystal finally nucleated in the undercooled melts. Up to now the short-range order of clusters in the undercooled melts can not be directly measured. Most considerations are based on theoretical models [12-16] using the principle of lowest energy. The speculations by Frank[17] about a possible preference of an icosahedral short range order in undercooled melts have recently been supported by a large number of computer simulation studies [12-14, 18, 19] and by investigation on free atomic clusters in mass spectra [7, 8, 20]. Icosahedral order implies fivefold symmetry, which is incompatible with the translational long range

order of a crystal. It also means that icosahedrally ordered atoms must be separated and rearranged during crystallization [4]. This additional barrier' against crystallization of the undercooled melt has been earlier referred to as responsible for the large undercoolings obtained on pure metals by the droplet-dispersion technique [6, 21, 22].

In the present work, different kind of extrinsic clusters are intentionally introduced onto undercooled melts of $\text{Ge}_{74}\text{Ni}_{26}$ alloy in order to get some information about the relationship between clusters and the nuclei. Nucleation happened as a result of agglomeration among clusters in the undercooled melt and externally introduced. Analyses of the effects of interfacial energy on the structure of the clusters at different undercoolings present an explanation of the transformation from clusters to nuclei during crystallization. Before nucleation atoms in the clusters tend to be packed more closely than they are in the crystal after nucleation. The higher the undercooling (the bigger the clusters in the undercooled melt), the less closely the atoms are packed in the clusters. The clusters are possible to be changed into nuclei only after the structure of them are evolved to the corresponding crystal structure with increasing undercooling.

2. Experimental

$\text{Ge}_{74}\text{Ni}_{26}$ alloy was selected to do the nucleation experiments, mainly because it has an appropriate melting temperature (about 100 K lower than that of pure Ge) to satisfy the high viscosity requirement of the molten B_2O_3 flux which was selected to safely sustain the sample and separate the sample from the bottom surface of a specially-designed shallow crucible, as shown in Figure 1. It is also because this alloy has a high resistance to oxidation and can be easily undercooled. Ingots of about 1g in weight

were prepared by arc-melting from 8 nines pure Ge and 5 nines pure Ni constituents. Clusters of Si, Ni and Cu can be produced through sputtering the corresponding Si, Ni and Cu targets with ion beam. In order to easily compare the effects of different kinds of clusters on nucleation, the sputtering parameters were selected as the same for the three different elements. The size of the clusters sputtered from the targets is possible to be estimated by the etching rate of the targets or by the depositing rates on a substrate. Direct measurement of the cluster size is impossible. The reasons to select Si other than Ge element to

produce clusters are that Ge is too expensive to make a target, and that both elements have the same crystal structure as well as similar properties. At the vacuum of 10^{-4} Pa, the sample was heated by electric resistance to 1223 K in 20 minutes and kept at this temperature for 25 minutes, then cooled by decreasing or even cutting down the electric current. In order to avoid the heterogeneous nucleation from the crucible walls, a layer of B_2O_3 flux was put in between the sample and the crucible. The cooling profiles were directly measured by a set of thermocouples just beneath the sample.

3. Experimental results

Undercooling experiments without triggering by extrinsic clusters were first done to check the undercooling ability of the samples. The largest undercooling obtained is 205 K, corresponding to a nucleation at the temperature of 904 K, as shown in Figure 2. Only one exothermic peak exists on the curve. According to the phase diagram [23], only a part of the melt of the alloy will first be transformed into primary phase (Ge), then the left part into eutectics (Ge + GeNi) during solidification. Examination of the microstructure reveals the existence of both the primary phase and the eutectics. So, on the corresponding cooling curve, recalescence represents the primary phase transformation whereas the plateau after recalescence represents the eutectic transformation. In Figure 3, the primary phase Ge exhibits a non-faceted dendritic morphology.

After the sample was kept at the undercooling of 166 or 136 K for 5 minutes, clusters of Si were introduced onto it. The cooling curves, as shown in Figure 3, exhibit

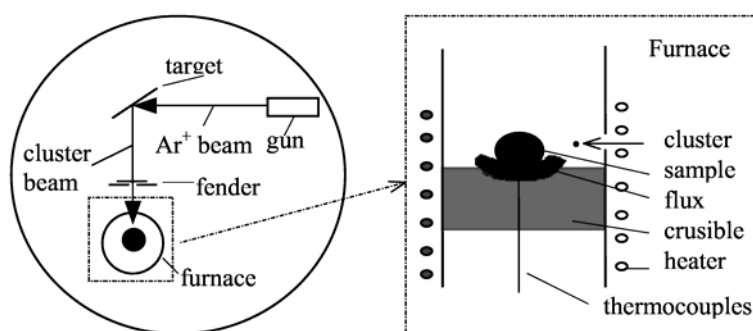


Fig.1. Schematic diagram of the facility for cluster-induced nucleation experiments. Clusters produced by ion beam sputtering of the target are introduced onto the undercooled melt to induce nucleation. The left part is a vertical view of the facility and the right is a front view of the furnace.

sudden rises just following the triggering operation. The undercooling was about 40 or 70 K smaller than that without triggering, 205 K. An earlier onset of nucleation happened when clusters were introduced. It can be concluded that extrinsic clusters of Si can be used as triggers to induce nucleation of undercooled $Ge_{74}Ni_{26}$ alloy melts. An important achievement presented here is that nucleation is induced by small clusters other than triggers with macrosizes. In earlier studies of nucleation in a undercooled melt using triggers with macrosizes, the levitated melt suffers from mechanical impacts [24]. Mechanical and thermal influences from the triggers are removed in the present experiments. It is particularly noteworthy that it is impossible for clusters to form a film on the undercooled melt within a very short time (the fender is closed immediately following the opening operation). Considering the high

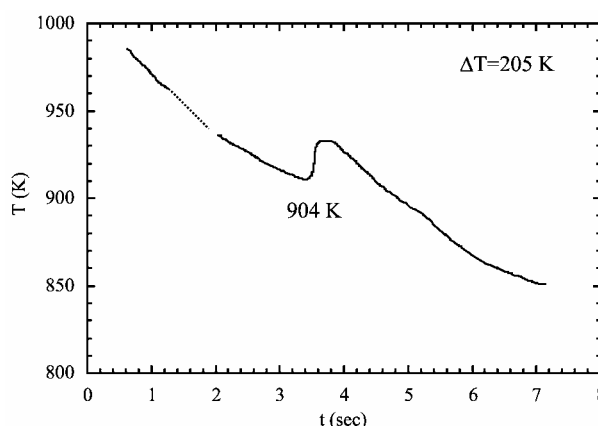


Fig.2. Temperature and time profile of the sample during continuous cooling and without triggering by clusters. Nucleation takes place at 904 K corresponding to an undercooling of 205 K

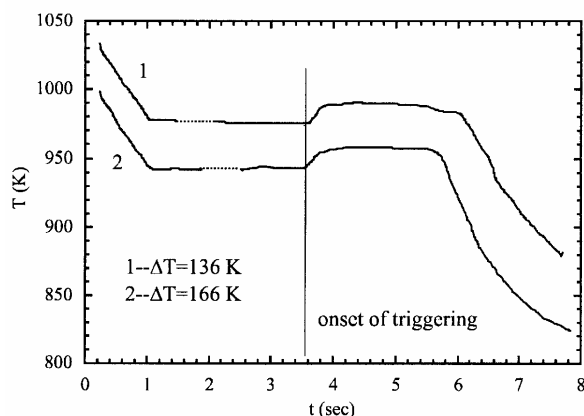


Fig.3. Cooling curves of the sample triggered by Si clusters at definite undercoolings, $\Delta T = 166\text{K}$ and $\Delta T = 136\text{K}$. Nucleation is induced immediately after the clusters are introduced

temperature and the convection in the melt, the possibility for the formation of detectable two-dimensional agglomeration only from the introduced clusters is even smaller. Further experiments on the deposition of the clusters on a Si substrate as well as on a quartz plate under the same sputtering parameters shows that agglomeration of clusters introduced did not reach the size large enough to be considered as heterogeneous nucleation site.

During continuous cooling, different kinds of clusters were introduced onto the sample respectively. The cooling curves are shown in Figure 4. For each of them there are two times of

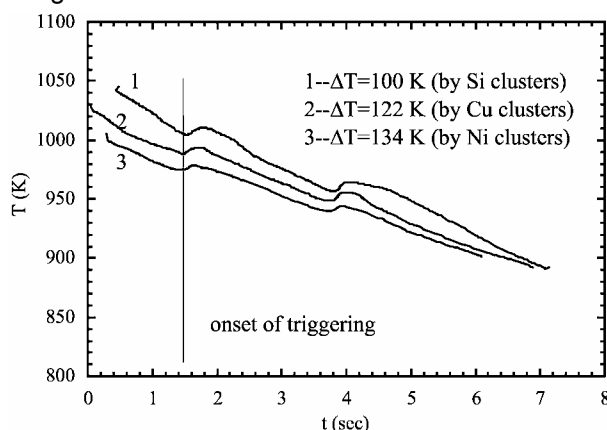


Fig.4. Cooling curves of the sample triggered by different kind of clusters during continuous cooling. Nucleation takes place at the undercooling of 100, 134 and 122 K when triggered by Si, Ni and Cu clusters respectively

recalcescence, the first is to the primary phase and the second to the eutectics. The first one is of particular importance because it indicates the

beginning of the phase transformation, which has direct relation to the undercooling reached. The undercooling level is specified by the difference between the equilibrium melting temperature and the temperature at which nucleation starts on the first time of recalcescence. The second, however, is not so important as the first one in the present studies on undercooling because it is influenced by the latent heat released during the first recalcescence. The term "nucleation" in the following text refers to the first one. When triggered by different clusters, the sample exhibits different onset temperature of nucleation, 1009, 975 and 987 K for Si, Ni and Cu clusters respectively, which are 105, 71 and 83 K higher than that without triggering, 904 K.

4. Discussion

4.1 Curvature effects on the structure of clusters and nucleation in undercooled melts

From the above experiments, it can be concluded that extrinsic Si clusters can be used to induce nucleation in undercooled $\text{Ge}_{74}\text{Ni}_{26}$ melt. In order to analyze the influence of clusters on nucleation we first simply refer to the classical nucleation theory, in which the critical radius r^* of the nucleus is expressed as follows [3]:

$$r^* = \frac{2\sigma T_m}{L\Delta T} \quad (1)$$

Where σ is the solid/liquid interfacial energy per area, T_m the equilibrium melting temperature, L the latent heat of fusion per unit volume, and ΔT the undercooling. Since the first phase transformation in the undercooled $\text{Ge}_{74}\text{Ni}_{26}$ melt is to the primary phase Ge, the properties of pure Ge can be used to estimate the critical nucleus size. σ is 0.32 J/m^2 [24], L is $3.68 \times 10^4 \text{ J/mole}$ and T_m is 1210 K [25]. At the undercooling of about 200 K, r^* can be calculated as 14 \AA , consisting about 800 atoms in the critical nucleus. On the other hand, we can also estimate the largest size of the clusters in the cluster beam sputtered from the target. With the same parameters a Si film was also deposited on a Si substrate and the depositing rate of the film is 1.2 \AA/s . Accordingly it can be estimated that the largest clusters in the cluster beam sputtered from the target were in the order of several tens of atoms at the very best. In comparison with the size of the nuclei, one cluster could not be directly acted as a critical nucleus to cause nucleation, because it did not reach the size of the critical nucleus. Therefore we can deduce that nucleation was caused by

the agglomeration among the clusters, introduced externally and existed originally in the undercooled liquid. No matter what kind of agglomeration, among extrinsic clusters or with clusters originally in the undercooled melts, a question is raised: why clusters with a size large enough (through agglomeration) can cause nucleation?

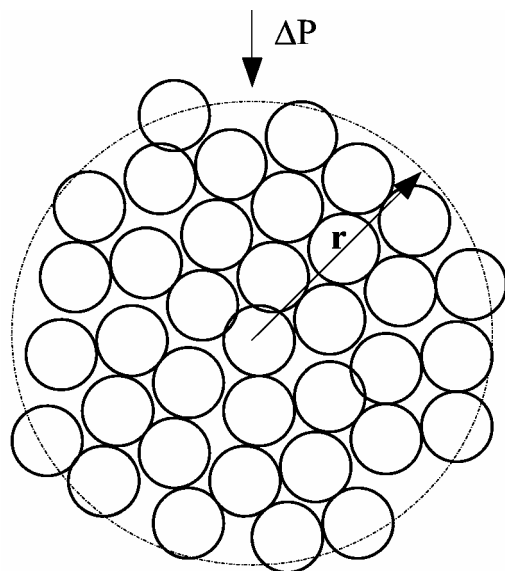


Fig.5. An additional pressure exists on the cluster because of the curvature effect. The pressure is directly related the cluster size and the interfacial energy per area

If the history of the cluster formation is checked from the very beginning, i.e. clusters are developed from 1, 2, 3,----- atoms, it is reasonable to consider that atoms are compacted in the closest way when clusters are extremely small, just as the result of computer simulation [1, 7-9, 20]. However the crystal, which will nucleate from the melt and which is at least in the size of nano-meter, always presents a definite structure. Accordingly, there is a transition from closely-compacted structure to crystal structure with increasing the cluster size. The formation of nuclei from clusters is, therefore, interesting to be examined.

The structure of an ensemble of atoms is determined by atomic interaction potential among the atoms, which has direct relation to temperature. The temperature influence on the structure of clusters in liquid is still unclear. But one thing is clear that the cluster size is increasing with increasing the undercooling. In the cluster scale, the curvature effect is exposed and may play the most important role on the structure of the clusters just as previous studies on nucleation phenomena [3]. In the following

paragraphs the curvature effects on cluster structure is analyzed.

Assuming, for simplicity, a sphere-like geometry of the clusters in the undercooled melt, the change in free energy, ΔG , during the formation of a cluster of radius, r , can be written as the sum of two contributions:

$$\Delta G = -\frac{4}{3}\pi r^3 \Delta G_V + 4\pi r^2 \sigma \quad (2)$$

Where ΔG_V is the volumetric free-energy difference per volume. The first term is the volume term and the second the interface term. Normally, the value of interfacial energy per area is influenced the cluster size, the undercooling, etc. and cannot be treated as constant. The traditionally used definition about the interfacial energy is hardly correct when it is directly extended to the cluster scale. However, to qualitatively analyze the curvature effects on the transition from cluster to nuclei it is still appropriate. In order to study the influence of the interfacial energy on the structure of the clusters, Gibbs' treatment of equilibrium between a solid and a liquid separated by a curved interface can be written as,

$$\Delta P = 2\sigma / r. \quad (3)$$

The influence of the interfacial energy on the cluster can be expressed as a pressure, ΔP , which acts on the surface of the cluster as shown in Figure 5. In the cluster scale, this pressure is extraordinarily high because the interface-to-volume ratio is very large. It is, for example, 2×10^9 Pa when r and σ are selected as 5 \AA and 0.3 J/m^2 respectively. It is about 20 times larger than that of the smallest crystals that are normally thought to be in the scale of about 10 nm. Such a high pressure is quite possible to cause the atoms in the cluster to be packed in the closest ways, such as icosahedron, octahedron, fcc, hcp, etc [7, 8, 20], most likely in the short range of icosahedrons when the clusters are extremely small. With increasing of the cluster size, or with increasing of the undercooling, the pressure will decrease at a very high rate as shown in Figure 6. As the pressure is lowered with the increase of the cluster size, clusters will correspond to a less densely-compacted structure. As a result, clusters with different sizes correspond to differently closely-packed states. So, there is a structure relaxation, or evolution, with the increase of the undercooling. When relaxed to some extent, the corresponding crystal structure may possible to appear if the undercooling is high enough.

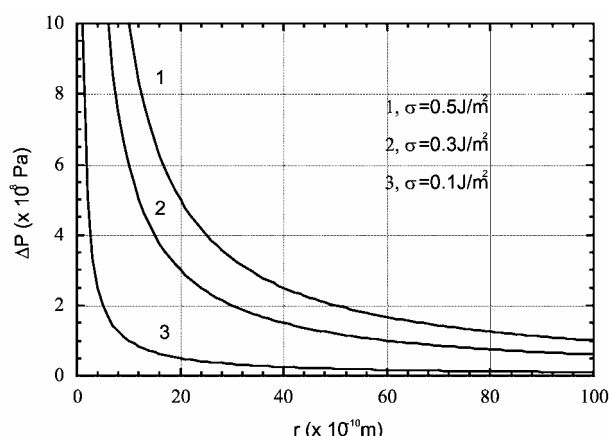


Fig.6. Relationship between ΔP and the radius of the cluster. For the smallest crystals, for instance in the size of 10 nm in diameter, the pressure is about 20 times as large as that of the cluster with the diameter of 5 Å

The above analyses about cluster evolution are in agreement with the previous computer simulation results [1, 7-9, 20, 26]. Computer simulation based on the calculations of the lowest energy content of ensembles of atoms, which are thought to be characterized by hard spheres, predicts a space frustration for a closely-packed cluster at a critical size, at which the energy gain due to icosahedral packing is completely consumed by the energy loss due to space frustration. The present prediction about the possible evolution in cluster structure is a strong support to the frustration point of view.

In fact, the structure change before nucleation was also pointed out by Herlach and Holland-Moritz to explain the high undercooling ability of metallic melts [1, 4]. Instead of the gradual change of the structure with increase the cluster size, a abrupt break-up of the icosahedral short-range order in the undercooled melt is predicted. Just as analyzed in the present work, however, this is not a abrupt break-up of the clusters. At different size, the clusters correspond to different closely-packed state. Only when the clusters are large enough (at a critical size), the cluster structure is corresponding to the crystal structure, and nucleation happens only when the clusters are larger than the critical size.

In metallic melts, structure fluctuation happens instantly. The size of the clusters at any moment is mainly determined by temperature. With decreasing temperature, the size of the clusters is increased. Nucleation happens only after clusters reach a critical level at which clusters can take the same structure as in crystals that will nucleate in the melt. Accordingly, metallic melts can be deeply

undercooled [6] until the clusters can be relaxed to this extent, provided there are no heterogeneous bases in the undercooled melt. When the cooling rate is big enough, cluster relaxation as well as nucleation can be avoided, and the amorphous phase [11], which is thought to be a kind of frozen liquid, will be formed. Sometimes nuclei are formed by relaxation but can not further grow into macroscopic crystals because of kinetic reasons. These nuclei will be kept in the amorphous phase, named as quenched-in nuclei [27].

When extrinsic clusters of Si were introduced into Ge-Ni alloy melts in the present experiments, clusters with a larger size were produced by cluster agglomeration. Hence a deep reduction of the pressure, ΔP , took place as a result of increasing of the cluster size, which further led to the structure relaxation. When the clusters relaxed to some extent and the crystal structure was formed consequently, nucleation was possible to take place. If we empirically consider the structures of the clusters externally introduced and originally existed in the undercooled melt are different from that of the crystal structure of Ge, structure relaxation is the most reasonable explanation to the formation of nuclei due to cluster agglomeration.

Structure evolution in clusters is a complicate process that is correlated to temperature, the type of the element, atomic bonds, etc. Further theoretical calculation and direct experimental examination is still needed. The above prediction about the relaxation in clusters before nucleation is not contradict to the classical nucleation theory. In fact it is a supplement to the classical theory, which has a shortcoming to describe the stage before nucleation. Nuclei are not directly formed from the clusters due to the incompatibility of the structures, but formed as a result of cluster relaxation with increasing of the cluster size, or in other words, with decreasing of the temperature. After the clusters are relaxed enough and the atoms in the clusters can occupy the positions like in the corresponding crystal structure, nucleation is possible to take place.

Up to now, it is impossible to directly measure the structure of the clusters both in the undercooled melt and in the cluster beam. Efforts to study the structure of clusters are still going on.

4.2 Influence of the cluster type on nucleation

When Si clusters were introduced into the undercooled melt, larger clusters were formed by

agglomeration among Si clusters introduced and the original clusters in the melt. It is plausible to attribute the influence of Si clusters on the nucleation of Ge to the agglomeration of clusters because of the good wetting ability between Ge and Si clusters. However, the influence of Ni and Cu clusters on nucleation of the primary phase Ge should be different from that of Si clusters. It was expected that induction of nucleation of Ge crystals should be much more difficult for Ni and Cu clusters. The difference in nucleation onset temperature when different clusters were introduced in the present experiment, however, was not as large as expected, only about 20 to 30 K. In fact, under the same sputtering parameters, the size of the Ni and Cu clusters was more than one times larger than that of the Si clusters. If the size of the clusters is taken into account, this small difference is still reasonable.

The fluctuations of density and concentration in the undercooled melt give rise to fluctuations of the structure of the clusters. In the undercooled Ge-Ni alloy melt, different kinds of clusters fluctuated at any moment. Clusters of Ge, Ni as well as a mixture of both elements appeared randomly. When extrinsic Ni and Cu clusters were introduced into the undercooled melt, the local equilibrium of the structure fluctuation at the place where the clusters were introduced was disturbed instantly. Larger clusters of Ge was possible to be formed even though they were not as a direct result of cluster agglomeration. Nucleation happened as an indirectly catalytic effect from the Ni and Cu clusters externally introduced.

5. Conclusion

Cluster-induced nucleation was successfully done. At a definite undercooling of 166 or 136 K, clusters of Si can be used to induce nucleation of undercooled $\text{Ge}_{74}\text{Ni}_{26}$ alloy melts. During continuous cooling, the onset temperature of nucleation was 1009, 975 and 987 K when triggered by extrinsic Si, Ni and Cu clusters respectively, much higher than that without triggering, 904 K. The influence of the introduced clusters on nucleation is from interaction among the clusters originally existed in the undercooled melt and the clusters introduced. The agglomeration of clusters led to the formation of clusters with a larger size. Relaxation of the structure with increasing of cluster size led to the nucleation of the crystalline phase.

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