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ABSTRACT

Pure nickel and two nickel-copper alloys (Ni-10 at.% Cu and Ni-50 at.% Cu) containing 50 appm preinjected helium have been irradiated with 14 MeV nickel ions at a constant homologous temperature of 0.45 T_m. The radiation induced crystal defects have been analyzed by TEM with samples prepared in cross-section. In the helium preinjected region of the pure nickel specimen, a substantial density of voids with an average diameter of 35 nm was observed. The nickel-copper alloys were found to contain only a high density of small helium bubbles (under 5 nm in diameter) and dislocation loops. The density of both dislocation loops and helium bubbles increases with the increasing copper content, and the size decreases with increasing copper content. The observed resistance of the nickel-copper alloys to void formation regardless of the presence of helium bubbles, is considered to be the result of local clustering of like atoms.

INTRODUCTION

Radiation induced void swelling is one of the serious material problems to be solved for the proposed fusion reactors[1]. To better understand the mechanisms controlling void formation process, pure metals and simple alloys are often chosen for radiation damage studies although they are unlikely to be used as fusion reactor materials. Ni-Cu alloys have been shown to be very resistant to void swelling under neutron[2], ion[3-6] and electron[7] irradiations in the past decade. Such an observation is very significant because the alloy system forms a complete solid solution over the entire composition range and voids can easily be produced in both pure nickel and copper in the presence of certain gas atoms. Helium is a transmutation product in fusion reactor materials due to (n,α) reactions and it is also known as a void nucleation agent. Zinkle et al.[8] injected 200 appm helium into nickel, copper and three Ni-Cu alloys at a homologous temperature of 0.65 T_m, and found nothing anomalous concerning helium bubble growth in the alloys which would explain the suppression of void swelling. Other than the above study, the effect of helium in Ni-Cu alloys has not been carefully investigated, even though some of the previously irradiated samples contain a certain amount of helium[2, 3]. The objective of this study is to determine if preinjected helium would promote void formation in Ni-Cu alloys during heavy ion irradiation. A heavy ion irradiated pure nickel specimen with helium preinjection is included in the study for the purpose of comparison.

EXPERIMENTAL

The pure nickel specimen used in this study came from a degassed Marz grade (99.995 wt.% pure) sheet which contains 75 appm oxygen. Our previous results showed that at this residual oxygen level, the effect of preinjected helium on void formation is more pronounced than in the as-received foil which contains 180 appm oxygen[9]. This is because oxygen is also found to be a void stabilizer[9,10]. Two Ni-Cu alloys, Ni-10Cu (at.%) and Ni-50Cu were fabricated from Marz grade Ni and Cu (99.999 wt.% pure) by arc melting followed by a homogeneity treatment in flowing argon at 1000°C for 24 hours. Vacuum fusion analyses performed by Los Alamos National Laboratory indicated that the oxygen content in the alloys was about 100 appm. The ingots of the alloys were cold rolled with intermittent annealing in flowing argon at 800°C to 0.5 mm thick foils, which were then mechanically polished with 0.05 μm alumina abrasive.

Helium ions with energies between 200-400 keV were injected into the two Ni-Cu alloy samples at Oak Ridge National Laboratory and the pure nickel specimen was injected earlier with 200-700 keV helium using the University of Wisconsin 700 KV Accelerator Facility. The helium injections were all performed at ambient temperature at a dose which gave an average concentration of 50 appm in the injected region.

The samples containing injected helium were then irradiated with 14 MeV Ni^{3+} ions at the University of Wisconsin Heavy Ion Irradiation Facility with a flux of ~ 3×10^{16} Ni^{3+}/m^2s at the constant homologous temperature, T/T_m=0.45, i.e. 500°C, 485°C and 425°C for pure nickel, Ni-10Cu and Ni-50Cu respectively. The reason for choosing this homologous temperature for irradiation is that voids are known to form only in the temperature range of 0.3-0.6 T_m. At lower temperatures, vacancies are not mobile enough to move together to form voids and most of them will recombine with a mobile interstitial atom. When the temperature is higher than 0.6 T_m, the equilibrium vacancy concentration is very high, which makes the vacancy supersaturation insufficient for void nucleation and growth. The irradiation doses were decided according to Monte Carlo calculations by the TAMIX code[11]. The pure nickel specimen received 3 dpa at the depth of 1 μm, the Ni-Cu alloy samples received 5 dpa at the same depth. The calculated displacement damage (by 14 MeV nickel ions) and the injected ion distributions (14 MeV nickel ions and helium ions with the energy range used during preinjection) in pure nickel and Ni-50Cu are shown in Figure 1 and Figure 2 respectively. The separation of the preinjected helium range from the injected nickel ion range allows their effects to be separated. The appm helium/dpa ratio at the helium injected region in this study is around 10 to 15, which is close to the ratio for potential fusion reactor materials[1].

After irradiation, the samples were prepared into cross-section TEM specimens[12], so that the entire ion damage range could be studied. TEM observation was performed under a JEOL TEMSCAN-200CX electron microscope with attention mainly focused at the helium injected region.

RESULTS

Figure 3 (A), (B) and (C) are the cross-sectional TEM micrographs showing the entire ion damaged range in the three irradiated samples. During preparation of the cross-section TEM specimens, the original surface of irradiation has been electroplated with nickel, so it becomes an interface in the micrograph. It should be mentioned that a surface layer of up to 0.3 μm thick was removed from the original surface before electroplating to insure good bonding at the interface. Therefore, the actual depth from the irradiated surface is about 0.3 μm more than the depth marked in the cross-sectional micrographs. The micrographs in Figure 4 were taken at a higher magnification from each specimen at the actual depth of 0.6-1.0 μm, where the preinjected helium is present.

The defect structures in the three irradiated materials are distinctly different. In the irradiated pure nickel, the most obvious defect clusters are voids, although prismatic dislocation loops are also present. Comparing the result reported earlier[9] on the nickel containing the same amount of residual oxygen but without helium preinjection, it appears that the relatively high density of voids in the first 1.5 μm of the nickel specimen shown in Figure 3(A) is due to the presence of preinjected helium in that region.

In the two irradiated Ni-Cu alloy samples, dislocation loops constitute the major defect cluster. The loop density increased dramatically with the copper content, while the loop size decreased concomitantly. Perfect loops on {111} planes with $\vec{b} = a/2 \langle 110 \rangle$ and Frank loops enclosing a stacking fault with $\vec{b} = a/3 \langle 111 \rangle$ were both identified in Ni-10Cu, but only perfect loops have been identified in Ni-50Cu. The analysis of the interstitial/vacancy nature of the dislocation loops has only been performed on some of the larger loops in Ni-10Cu, both vacancy and interstitial loops have been identified. The density and size distribution of the loops are almost the same as the result of another previous study[6] on the irradiated Ni-Cu alloys with 5 MeV oxygen ion preinjection. Since the 5 MeV oxygen was implanted deeper in the samples, the similarity in the loop distribution means that the preinjected helium did not have the power to alter the defect characteristics in the alloys under our experimental conditions. However, when dislocations are tilted out of contrast, e.g. the specimen is tilted away from the strong diffracting orientation, small bubbles with diameters less than 5 nm are observed at the helium injected depth in both Ni-10Cu and Ni-50Cu as shown in Figure 5. The density of the helium bubbles in Ni-50Cu is an order of magnitude higher than that in Ni-10Cu, and the bubble size is larger in the latter. When comparing the size of the bubbles in the Ni-Cu alloys with the size of voids in pure nickel as shown in Figure 5(A), please note that Figure 5(B) and 5(C) have a much higher magnification. In addition to dislocation loops and bubbles, small black dot damages, some of which have been identified as stacking fault tetrahedra, are also seen in the irradiated Ni-Cu alloy samples. Figure 6 is a weak-beam dark-field electron micrograph showing the presence of stacking fault tetrahedra in the irradiated Ni-50Cu.

Table I. summarizes the major defect characteristics in the helium injected region of the three materials irradiated in this study. The volume swelling in the helium preinjected region of the nickel specimen is about 3.5×10^{-3}, while the swelling due to the formation of small bubbles in the Ni-Cu alloys is estimated to be at least one order of magnitude lower, even though the Ni-Cu samples were irradiated to a higher displacement damage level. Based on the data tabulated in table I, the residual vacancy/helium ratio in the voids or bubbles has been estimated to be 70 for the pure Ni sample, 1.5 for the Ni-10Cu sample and 3.5 for the Ni-50Cu sample.

DISCUSSION

The formation of helium bubbles in the Ni-Cu alloys is expected, because there are theoretical and experimental indications that helium tends to undergo spontaneous precipitation when implanted in metals, including the void resistant Ni-Cu alloys[8]. The interesting point of our results is that the resistance to void swelling of the Ni-Cu alloys is maintained even in the presence of small helium bubbles during irradiation. A simple calculation based on the ideal gas law and the assumption of equilibrium bubble pressure indicated that some vacancies must be trapped in the helium bubbles to achieve the bubble volume observed in this study. Nevertheless, the majority of the excess vacancies which survived recombination apparently did not go to the bubbles to cause growth into larger voids. Instead, they form dislocation loops just as if there is no helium available to help void nucleation. It is thought that this phenomenon can be explained by the mechanism first proposed by Mazey and Menzinger[3] in 1973, namely, that possible local clustering of like atoms might provide traps for vacancies and gas atoms in the Ni-Cu alloys. The mechanism has also been discussed in a recent publication[6] and it is extended here.

In a binary solid solution composed of elements A and B, local clustering is defined as having a reduced number of unlike nearest neighbors, or A-B pairs, than the number in a random solution[13]. The essential condition for that to happen is that similar atoms must attract each other more than dissimilar atoms in order to lower the free energy upon clustering, although the interaction is not strong enough for precipitation. In terms of interaction energies between pairs of atoms of the two atomic species, this condition can be expressed as $E_{AB} > 1/2\ (E_{AA}+E_{BB})$[13,14]. When the above condition is met, the short range order parameter α_1[15] should be greater than zero[13,15]. Vrijen and Radelaar[16], in 1978, systematically studied the short range order parameters for the Ni-Cu system using diffuse neutron scattering. Their results from the alloys quenched at 450°C, along with some of the measurements made by Aldred et al. in 1973[17] and Medina et al. in 1977[18], are plotted in Figure 7. The data indicated not only that local clustering does occur in the Ni-Cu alloys but also that the tendency for clustering is higher in a more concentrated Ni-Cu solid solution than in a dilute solution.

The boundaries of fine clusters of like atoms in the alloy may tend to trap vacancies and gas atoms to reduce the relatively high bonding energy and strain energy. When an abundance of this kind of trap is available, vacancy supersaturation cannot be achieved fast enough at each site for vacancy clusters to grow beyond the critical size of the void embryo before collapsing into dislocation loops. For the same reason, helium bubbles cannot draw enough vacancies to grow into larger voids. Since Ni-50Cu contains more such fine scale clusters, gas atoms and vacancies are distributed among more traps than in the case of Ni-10Cu, therefore, a smaller size and higher density of bubbles and dislocation loops result. The tendency for clustering also increases with decreasing temperature[16] and during irradiation[19], so that the higher density of bubbles observed in this study versus the relatively low density and alloy composition independent distribution of helium bubbles observed by Zinkle et al.[8], after injecting helium at 0.65 T_m without further irradiation, can also be understood.

CONCLUSIONS

Preinjection of 50 appm helium into Ni-10Cu and Ni-50Cu has little effect on promoting void formation by irradiation with 14 MeV nickel ions to 5 dpa, while preinjection of 50 appm helium results in copious voids in pure nickel by irradiation to 3 dpa at the same homologous temperature of 0.45 T_m.

Most excess vacancies precipitate into dislocation loops in irradiated Ni-Cu alloys regardless of the presence of small helium bubbles. The density of both dislocation loops and helium bubbles increases with increasing copper content, and the size decreases with increasing copper content.

The special swelling resistance of Ni-Cu alloys is considered to be the result of local clustering of like atoms.

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Table I. Major defect characteristics* in 50 appm helium preinjected Ni and Ni-Cu alloys following 14 MeV Ni ion irradiation

Material	dpa	Irradiation Temperature (°C)	Dislocation Loop density (m^{-3})	Dislocation Loop average size (nm)	Helium Bubble (or Void) density (m^{-3})	Helium Bubble (or Void) average size (nm)
Ni	3	500	$1x10^{20}$	15.3	$1.5x10^{20}$	35 (void)
Ni-10Cu	5	485	$1x10^{21}$	27.5	$3.0x10^{21}$	3.5
Ni-50Cu	5	425	$7x10^{21}$	6.5	$3.0x10^{22}$	2.3

* Defect parameters in the table are measured from the region about 1 μm below the irradiated surface

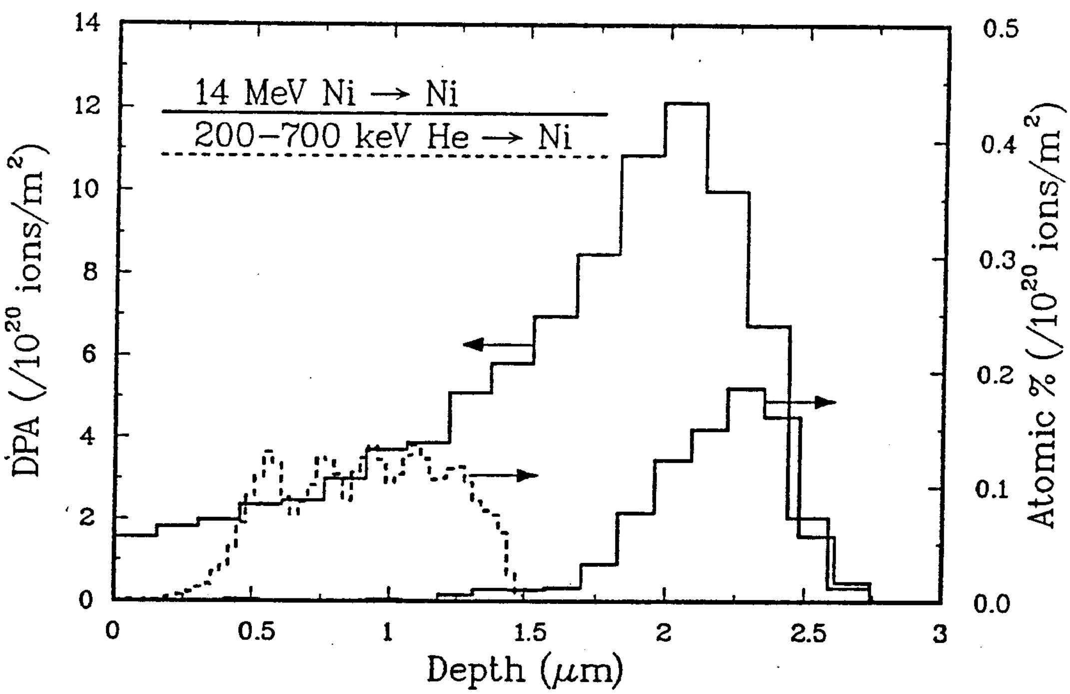

Figure 1. Displacement damage (by 14 MeV Ni ions) and injected ion distributions (14 MeV Ni ions and 200-700 KeV He ions) in pure Ni calculated by using the Monte Carlo code, TAMIX[11].

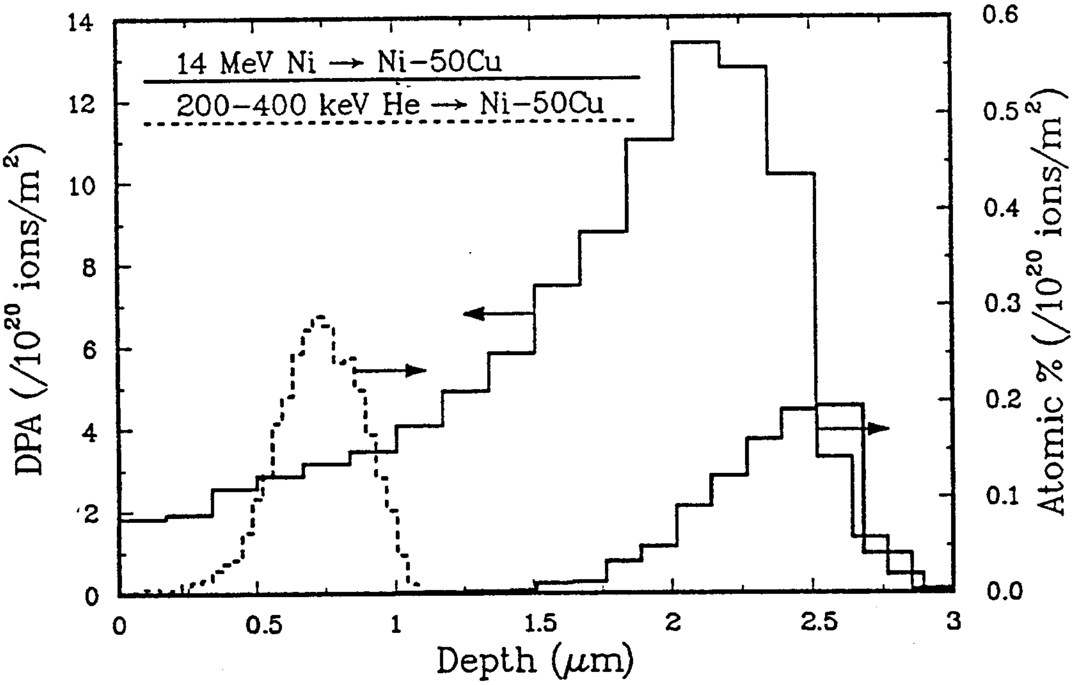

Figure 2. Displacement damage (by 14 MeV Ni ions) and injected ion distributions (14 MeV Ni ions and 200-400 KeV He ions) in Ni-50Cu calculated by using the Monte Carlo code, TAMIX[11].

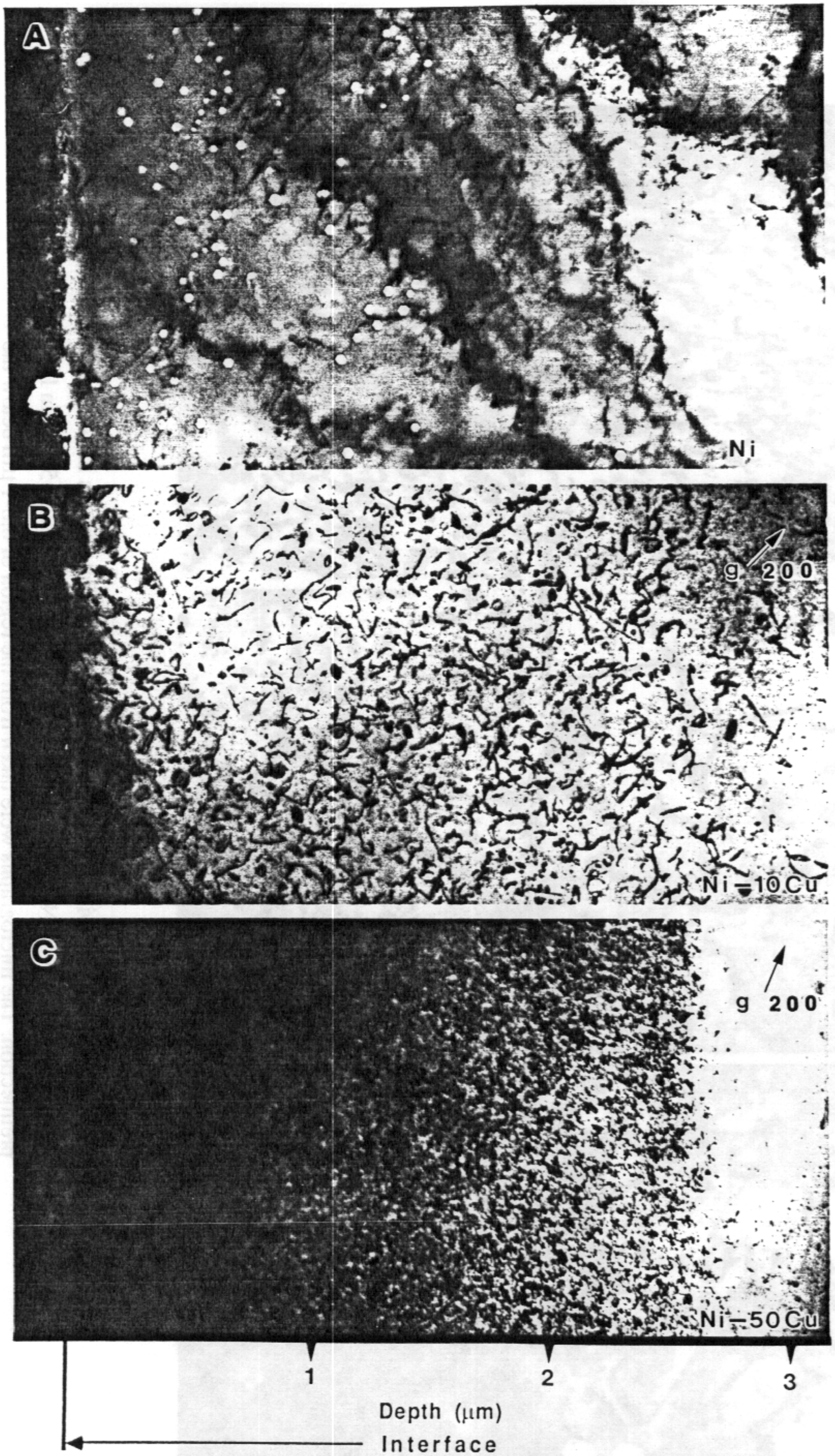

Figure 3. Cross-sectional TEM micrographs showing the entire ion damaged region in 14 MeV Ni ion irradiated (A) pure Ni (3 dpa at 1 μm, 500°C), (B) Ni-10Cu (5 dpa at 1 μm, 485°C) and (C) Ni-50Cu (5 dpa at 1 μm, 425 °C). 50 appm He (200-700 KeV for pure Ni, 200-400 KeV for the alloys) was preinjected at ambient temperature before Ni ion irradiation.

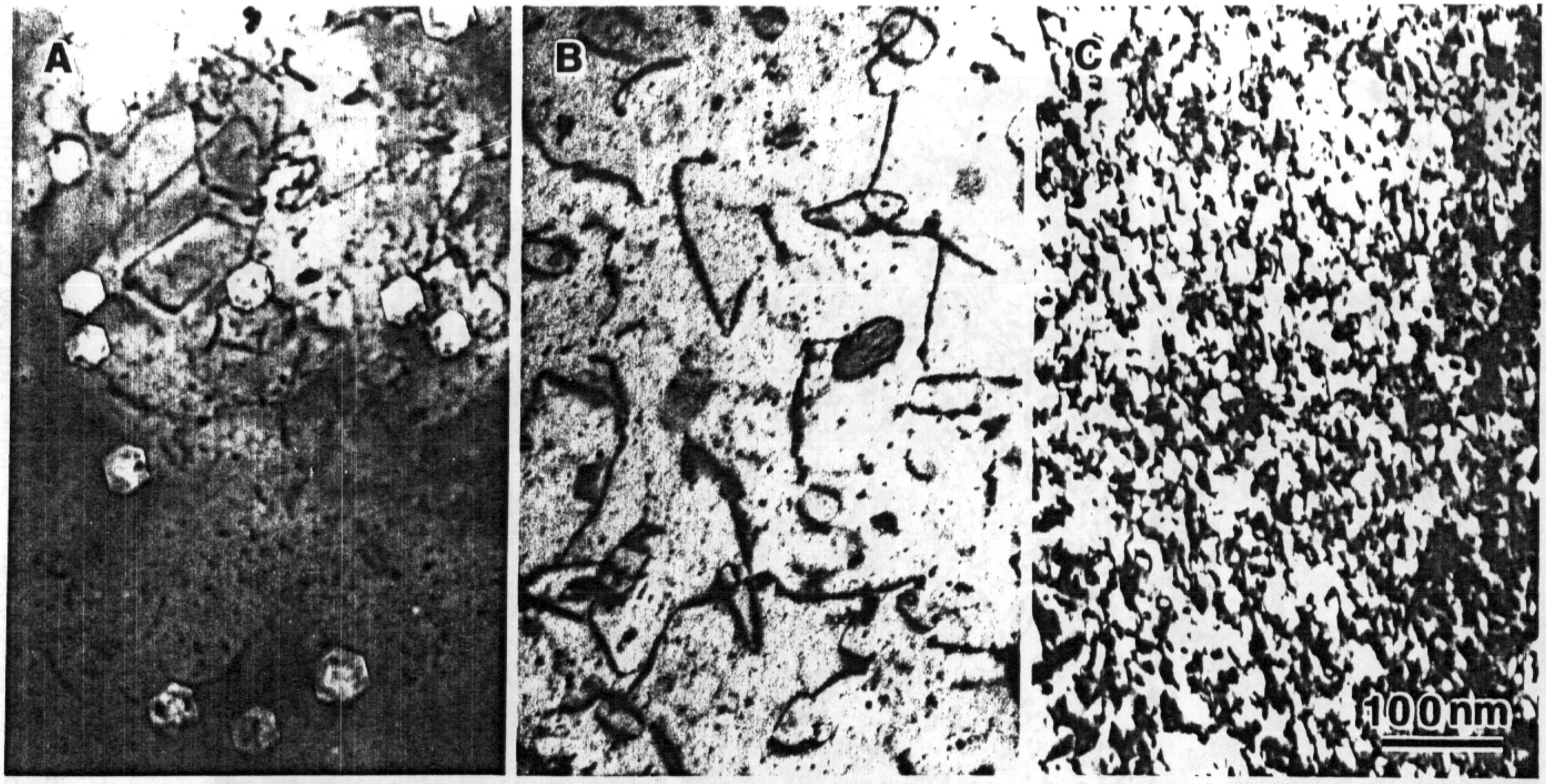

Figure 4. TEM micrographs showing the comparison of major defect clusters in 14 MeV Ni ion irradiated (A) pure Ni, (B) Ni-10Cu and (C) Ni-50Cu, all with 50 appm He preinjection. The micrographs were taken from the region of 0.6-1 μm below the irradiated surface (g=[200]).

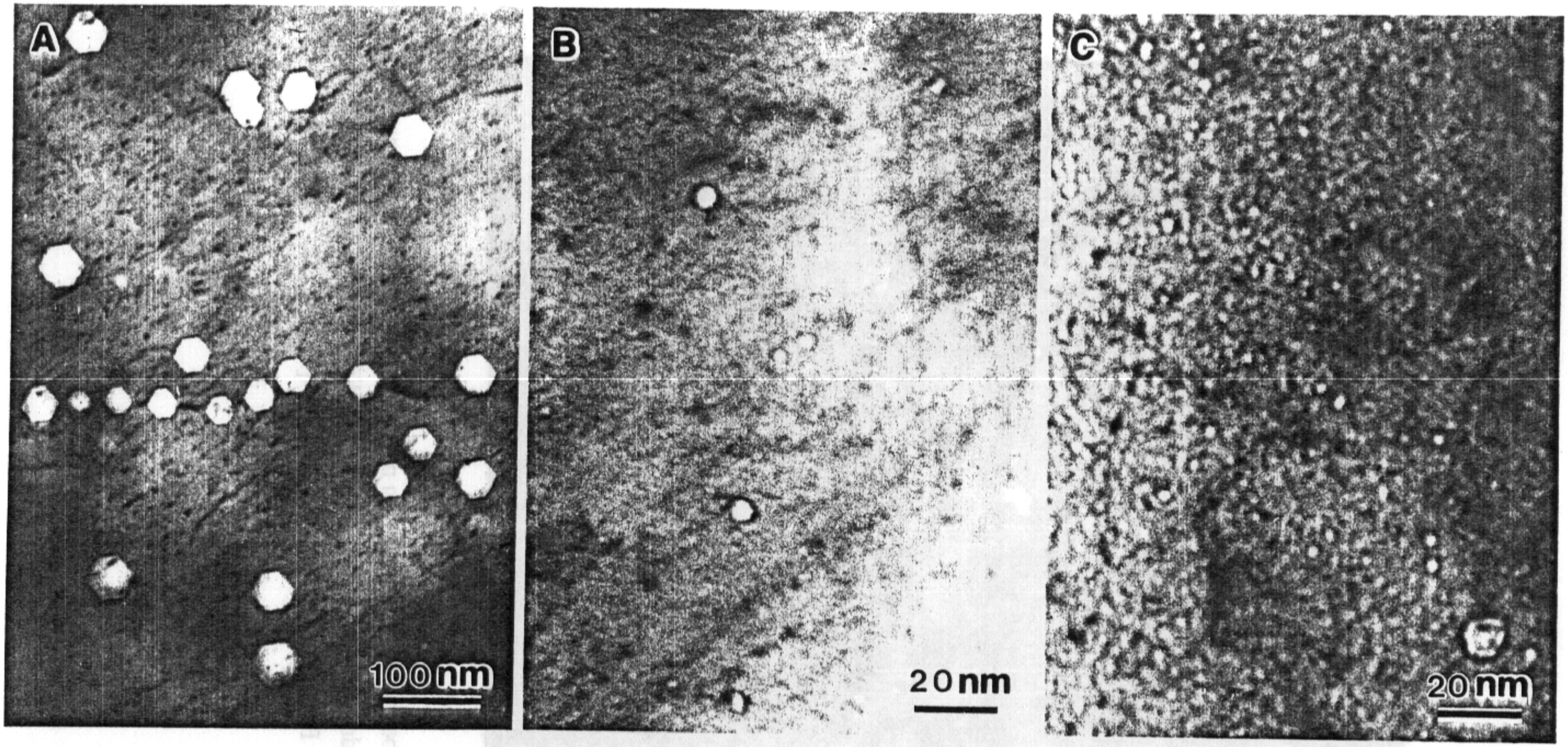

Figure 5. Low contrast TEM micrographs showing the comparison of the effect of preinjected He in 14 MeV Ni ion irradiated (A) pure Ni, (B) Ni-10Cu and (C) Ni-50Cu. The micrographs were taken from the region of 0.6-1 μm below the irradiated surface.

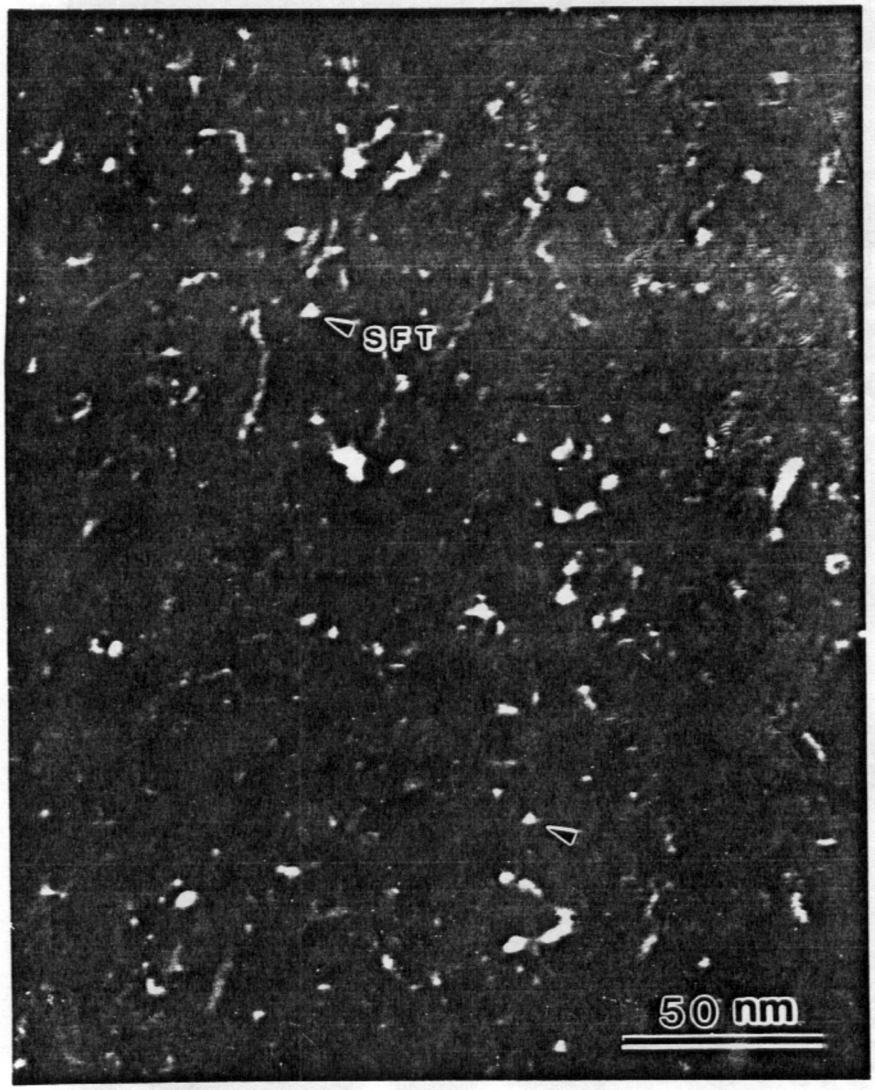

Figure 6. Weak-beam dark-field electron micrograph showing the presence of stacking fault tetrahedra (SFT) in 14 MeV Ni ion irradiated Ni-50Cu (50 appm He preinjection, 5 dpa). Foil normal is close to [011], g=[200].

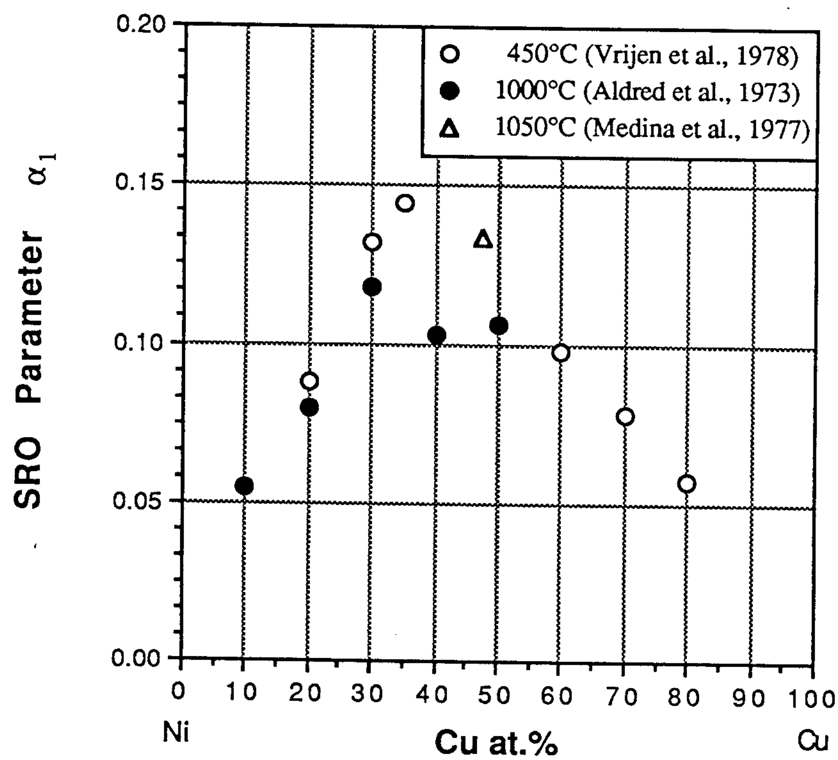

Figure 7. Short range order parameter α_1 for Ni-Cu alloys measured by Vrijen et al.[16], Aldred et al.[17] and Medina et al.[18] with diffuse neutron scattering after quenching from various temperatures.