Although it is not possible to describe the exact mechanism for the production of Z_2 centres which reveals the second order reaction of dipoles, it is considered that the movement of divalent ions or their complexes during X-irradiation is required in order to give rise the second order reaction. With respect to this problem, it has been reported that the divalent metal aggregates as well as showing decomposition of dipoles during X-irradiation at room temperature [7], which seems to suggest the free movement of dipoles as well as impurity ions and/or vacancies when the sample is irradiated by X-rays at room temperature.

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H. -J. KOS
R. NINK
Physikalisch-Technische Bundesanstalt,
Institut Berlin

N. TAKEUCHI
Faculty of Technology,
Kanazawa University,
Kodatsuno 2-40-20,
Kanazawa (920),
Japan

Intergranular embrittlement caused by the precipitation of M_6C carbide containing silicon

It was found that a nickel alloy with the following base composition (wt%)

C	Si	Cr	W	Mo	Ti	Al	Ni
⩽ 0.12	⩽ 0.6	13	6	3	2	2	Base

becomes embrittled when the silicon content approaches its upper limit. Therefore a series of alloys with silicon contents varying from 0.22 to 1.49 wt% were prepared. After quenching first from 1190° C and then from 1050° C, these alloys were aged at 800° C for 16 h. Fig. 1 shows the room temperature impact toughness of these alloys with a minimum at 0.5–0.6 wt% Si. This abrupt degradation in the impact property at 0.4–0.6 wt% Si and its subsequent recovery at a silicon content above 0.7 wt% was considered to be somewhat abnormal and therefore a thorough metallographic examination was carried out in order to clarify the behaviour of silicon in this type of alloy.

The embrittled alloy gives typical intercrystalline fracture appearances after impact testing. Microscopic examination of polished specimens shows the presence of many tiny particles precipitated at the grain boundaries along which cracking takes place. Electron microprobe analysis shows the enrichment of silicon at the grain boundary reaching about 7 to 8 times the average silicon content of the matrix. In order to ascertain the nature of the grain boundary precipitates, an electron optical examination of the extraction replica, made directly from the intergranular fracture surface, was carried out.

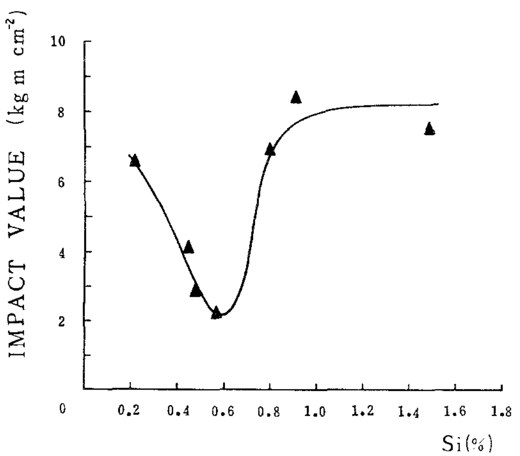

Figure 1 Variation of impact toughness with percentage silicon in a nickel alloy, measured at room temperature.

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The intergranular precipitates in an alloy with 0.45 wt% Si have two obviously different morphologies, either appearing as large thin flakes or as small round particles. Selected area electron diffraction analysis confirms the former as M_6C and the latter as $M_{23}C_6$. With increasing percentage of silicon in this alloy, the amount of M_6C increases at the expense of $M_{23}C_6$ and the M_6C flakes appear to be interconnected like semi-continuous films (Fig. 2) thus causing severe embrittlement of the grain boundaries. However, as the percentage silicon of the alloy reaches 0.7 wt% and above, coagulation of M_6C takes place rapidly and M_6C appears now mostly as round particles (Fig. 3), therefore losing its embrittling effect. Meanwhile, the grain size was found to increase from ASTM No. 3–4 to No. 5–6 when the silicon content was increased from 0.4 to 0.9 wt%. This grain refinement noticeably increased the grain boundary area and therefore reduced the embrittling effect of the precipitation of M_6C. This explained why the impact toughness recovered gradually when the silicon content of the alloy was increased beyond 0.7 wt%. Obviously, it is the thin flaky morphology rather than the type of crystal structure of the intergranular precipitates that is of prime importance in causing this kind of intercrystalline fracture.

From the facts that silicon is enriched abundantly at the grain boundaries and that it promotes the formation of M_6C, it seems logical that silicon may enter M_6C as a constituent. In order to obtain the chemical composition of the M_6C carbide in this alloy the specimen was kept at 1050° C for 45 h to allow the M_6C carbide particles to grow to noticeable sizes so that an electron microprobe analysis could be made directly on these particles. The composition of M_6C was found to be $(\mathrm{Ni\,Si_{0.2}})_3(\mathrm{Mo_{0.25}W_{0.15}Cr_{0.4}})_3C$ or $M_{5.4}Si_{0.6}C$, similar to that obtained previously either in a nickel alloy [1] or in a steel (in the latter case M_5SiC) [2]. Thus it is clear that by incorporating itself into M_6C silicon promotes the formation as well as the coagulation of M_6C. The former has the effect of increasing the intercrystalline embrittlement while the latter decreases it. This is the reason why there is the anomaly of a sudden drop in impact toughness at 0.4–0.6 wt% Si.

Figure 2 Semi-continuous flakes of M_6C, extracted from an intergranular fracture (× 5250).

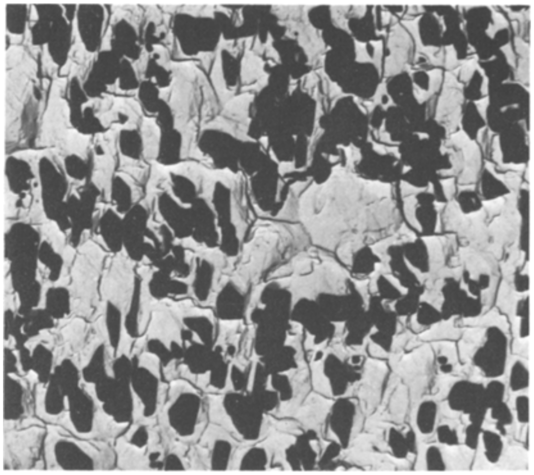

Figure 3 Round M_6C particles in an alloy with 0.91% Si, extraction replica (× 5250).

Both M_6C and $M_{23}C_6$ have an f c c lattice and also have similar lattice constants, the former being about 10.9 Å and the latter about 10.6 Å. Since this small difference in lattice constants (less than 4%) is comparable with the accuracy of ordinary selected area electron diffraction analysis, it is sometimes difficult to differentiate these two carbides merely by analysing the geometry of the electron diffraction pattern. Therefore it is necessary in this case to resort to an intensity analysis of the diffraction spots taking advantage of the fact that these two carbides have different space groups. The crystal structure of M_6C belongs to the Fd3m space group with a diamond glide plane d. All $hk0$ reflections with $h + k \neq 4n$ such as 2 0 0, 4 2 0, 6 0 0, etc., are forbidden.

Since such a glide plane does not exist in Fm3m, to which the crystal structure of $M_{23}C_6$ belongs, the above restrictions do not exist in this case. Furthermore, by calculating the structure factors for electron scattering of these two carbides it was shown that the reflections such as 4 2 0, 5 3 1, 6 0 0, etc., are of much higher intensities in $M_{23}C_6$ than in M_6C; on the other hand, reflections such as 4 0 0, 3 3 1, 5 5 1, etc., are of much higher intensities in M_6C than in $M_{23}C_6$. In spite of the effects of multiple diffraction which always exist in the case of selected area electron diffraction, one can still differentiate M_6C from $M_{23}C_6$ by means of these reflections. This may be a better criterion for the identification of M_6C than the condition of $h^2 + k^2 + l^2 = 4(2n + 1)$ given by Ohmori [3] because the latter is not generally valid. According to the latter criterion, 6 2 2 should be a weak reflection but in fact it appears as a medium one.

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X. M. GUAN
H. Q. YE
Institute of Metal Research,
Academia Sinica,
Shenyang,
The People's Republic of China.

TiO_2–SiO_2 glasses prepared from metal alkoxides

One of the advantages of preparing oxide glasses from metal alkoxides through hydrolysis and gelling rather than by the conventional melting method is that only relatively low temperatures are required [1, 2]. This technique, therefore, can be applied to the preparation of glasses which are difficult to obtain by a melting method because of their high melting temperatures.

The nature and properties of a gel, precursor for an oxide glass obtained from metal alkoxides through hydrolysis, has been shown to be affected by the added water and catalyst contents, the hydrolysis temperature and the solution pH [3, 4]. Fibres could be drawn from alkoxide solutions in the course of hydrolysis, when water was added in an amount insufficient for the completion of the hydrolysis, which made it possible to prepare glass fibres of the TiO_2–SiO_2, Al_2O_3–SiO_2 and ZrO_2–SiO_2 systems [5, 6]. On the other hand, homogeneous hydrolysis of metal alkoxides with excess water gave jelly-like masses suitable for obtaining non-particulate glasses. This indicated that excess water for the hydrolysis of metal alkoxides is an important requirement for making monolithic glasses from alkoxides, even though the rate of heating the gels and the porosity of the gels should also be controlled. The monolithic SiO_2 [7], Al_2O_3–SiO_2 [8] and B_2O_3–SiO_2 [9] glasses, so far, have been prepared from metal alkoxides.

In the present note, the metal alkoxide method for glass preparation was applied to the monolithic glasses of the TiO_2–SiO_2 systems on the basis of above considerations. The TiO_2–SiO_2 glasses containing TiO_2 up to about 10 wt% are known to show ultra-low thermal expansions [10]. With a

TABLE I Composition of the oxide glasses formed through the hydrolysis and gelling method

Specimen	Amounts of raw materials					Calculated composition of the oxide glass (wt%)
	$Ti(OC_3H_7)_4$ (g)	$Si(OC_2H_5)_4$ (g)	H_2O (g)	CH_3COOH (g)	C_2H_5OH (ml)	
1	0.65	20.42	90.0	0.06	80	3.0% TiO_2–97.0% SiO_2
2	1.08	20.02	90.0	0.06	80	5.0% TiO_2–95.0% SiO_2
3	1.73	19.37	90.0	0.06	80	7.9% TiO_2–92.1% SiO_2

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