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Effect of Transition Elements upon the Nucleation and the Morphology of Magnetite in Silicate Melts of Basaltic Composition

By

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with 1 Table, 4 Figures and 3 Plates

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Abstract: Effects of transition elements, Ti, Cr and Cu upon the nucleation and morphology of magnetite in silicate melts of basaltic compositon were examined. Crystallization of magnetite was carried out at $\Delta T = -10°C$ in the atmospheric condition. Quenched products are composed of magnetite, (plagioclase) and silicate glass. Examinations of the morphology of magnetite show that an addition of Ti and Cu with $K_{eff} < 1$, promotes the development of dendritic and/or skeletal morphologies, whereas Cr, with $K_{eff} > 1$, has a definite effect to decrease grain size and to increase the number of crystals. The results obtained were discussed in relation to σ^*, σ^{**} and K_{eff}.

Contents

I. Introduction

The process and mechanism of crystallization of minerals in silicate melt have long been a topic interest and much works have been done both theoretically and experimentally. Kirkpatrik (1975) has recently reviewed experimental works on dynamic crystallization of silicate minerals such as augite, diopside, olivine and plagioclase. Magnetite which is believed to be the eariest phase to crystallize in the silicate melts of basaltic compositions shows occasionally dendritic or hopper morphology in natural rocks (e.g. Basta and Shaalan, 1974; Haggerty, 1976; Takasawa and Hirano, 1979). However, such morphologies have not been produced experimentally, although several efforts have been made.

The morphology of crystals changes, in general, depending on the degree of supersaturation σ in solution growth. According to Sunagawa (1977, 1980), dendritic morphology appears under the supersaturation condition higher than σ^{**}, and skeletal (hopper) morphology between σ^* and σ^{**}, whereas polyhedral morphology bounded by flat faces below σ^*. The σ^* and σ^{**} are transitional supersaturation, where growth mechanism changes from dislocation controlled to two-dimensional nucleation growth mechanism, and from layer-by-layer growth mechanism to adhesive type growth mechanism, respectively. Thus dendritic morphology appears by diffusion controlled adhesive type growth, not by dislocation controlled layer-by-layer growth. According to SUNAGAWA (1980, 1981a), these morphologies are rare to meet among natural crystals, as compared to laboratorically produced crystals.

It is well known that impurities have striking effects both on nucleation rates and morphology of crystals. Impurities act as inhibitors for heterogeneous sites, which will result in drastic decrease in thermodynamic barriers for nucleation and drastic increase in the nucleation rates. They also give drastic habit change (numerous examples have been known for crystal growth in aqueous solutions, e.q. refer to BUCKLEY, 1951). Such changes have been accounted for in terms of epitaxial growth and/or the formation of two-dimensional complexes. Recently, the impurity effects on morphology have been analysed as due to the drastic change in edge free energies by impurities (SUNAGAWA, 1981b).

It is purpose of this paper to report experimental results on the effect of impurities upon both the nucleation rates and morphology of magnetite crystals grown in silicate melt of basaltic compositions. It has been found that skeletal morphology of magnetite is easily produced when the transition elements with $K_{eff}<1$, Ti and Cu, are added. It is also noted that the elements with $K_{eff}>1$, like Cr, have a marked effect upon the nucleation rates. Thus, partition of Ti, Cr and Cu between magnetite and silicate melt will also be discussed.

II. EXPERIMENTAL METHOD

Two basaltic compositions selected for the present experiment are shown in Table 1. Special grade reagents of SiO_2 (precipitated), Al_2O_3, Fe_2O_3, MgO, CaO, Na_2O_3 and MnO were used to prepare the starting materials. Transition elements of Ti(TiO_2), Cr(Cr_2O_3) and Cu(CuO) were added to the above two compositions in the ratios of 1.0,

TABLE 1. CHEMICAL COMPOSITION OF THE STARTING MATERIAL (wt. %).

	I	II
SiO_2	48.5	42.8
Al_2O_3	19.0	15.9
FeO	11.2	13.4
MgO	7.9	8.9
CaO	10.6	13.0
Na_2O	2.5	3.5
K_2O	0.2	2.0
MnO	0.1	0.5
Total	100.0	100.0

3.0, 5.0 and 7.0 wt.% of metals, respectively.

About 10 gram of mixtures were put in a platinum crucible and heated up to 1300°C in an electric furnace and kept for one hour under the atmospheric conditions. It was assured that the starting mixtures were completely melted. The melting temperature (T_M) of the two compositions without impurity is about 1210°C, determined by DTA experiments. Any significant change of the T_M, within the experimental error, was not observed by the addition of a small amount of the transition elements to the basaltic composition. After keeping the sample at 1300°C for one hour, the crucible was cooled down to 1200°C ($\Delta T = -10$°C) and kept for two hours followed by quenching in distilled water. All quenched products were examined under the microscope using both transparent and reflected light. All products of composition I are composed of magnetite, plagioclase and glass, whereas those of composition II of magnetite and glass. Chemical compositions were examined using JEOL (JXA-5A type) microprobe analyser.

III. RESULTS

It is found that different transition elements have different effects upon the size and morphology of magnetite crystals.

(1) *Titanium*

Addition of 1.0 wt.% Ti to the composition I causes development of dendritic form of magnetite. Fig. 1–A in Plate V shows beautifully developed dendritic magnetite coexisting with skeletal plagioclase. The dendritic character of magnetite becomes more conspicuous as the amount of Ti increases. However, pseudobrookite is formed when more than 3.0 wt.% Ti is added, and the amount of magnetite crystals decreases (see, Fig. 1–C in Plate V). In the case of composition II, magnetite crystals show less pronounced dendritic morphology than in the case of composition II. That is, when 1.0 wt.% Ti is added, magnetite shows skeletal rather than dendritic morphology. With increasing Ti content, the morphology transforms from skeletal to dendritic, and pseudobrookite appears above 3.0 wt.% Ti, when magnetite shows dendritic morphology.

(2) *Copper*

Addition of Cu promotes dendritic and skeletal morphologies. The dendritic morphology coexisting with skeletal plagioclase is more conspicuous in the runs of the composition I than those in the composition II. As is seen in Fig. 2–A in Plate V, addition of 1.0 wt.% Cu brings beautiful dendritic form which becomes more and more conspicuous with increasing Cu content (Fig. 2–B and C in Plate V). Above 5.0 wt.% Cu, the color of the coexisting glass becomes more and more reddish-brown keeping the dendritic morphology of magnetite almost unchanged.

Addition of Cu to the composition II also causes skeletal morphology (Fig. 3–A in Plate VI). With increasing Cu addition, the skeletal morphology becomes more marked up to 5.0 wt.% (Fig. 3–B in Plate VI). Above 5.0 wt.%, color of the coexisting glass becomes markedly reddish-brown keeping the morphology of magnetite almost unchanged.

(3) *Chromium*

When Cr is added, sizes of magnetite crystals diminish and the number of magnetite crystals increases drastically in both cases of compositions I and II. The average size of the crystals diminishes to less than 1/10 of that in the case of Ti and Cu for 1.0 wt.% Cr. As compared to the average size of almost 100 μm for 1.0 wt.% Ti, the size of magnetite becomes less than 10 μm when 1.0 wt.% Cr is added (see, Fig. 4–A in Plate VI). With increasing Cr content, the size diminishes further (Fig. 4–B in Plate VI). The crystal habit of these minute magnetite is obscure but the observation at higher magnification indicates polyhedral morphology.

(4) *Addition of two or three elements*

A) Cr+Ti, Cr+Cu and Cr+Ti+Cu

Any combinations containing Cr have a clear effect to decrease the size of magnetite crystals. Figs. 5–A and B in Plate VII show this effect clearly, due to the addition of Cr+Cu to the composition II, and Cr+Ti to the composition I, respectively. Fig. 5–C in Plate VII shows the result of addition of Cr+Ti+Cu combination. In all these figures, magnetite crystals show much smaller in size, and do not take dendritic nor skeletal morphology.

B) Ti+Cu

In Figs. 5–D, E and F in Plate VII, the results of addition of Ti+Cu (1.5 wt.% for the both metal) to the composition II and I are shown, which clearly show skeletal morphology accompanying flat faces. If these figures are compared with Figs. 1 and 2 in Plate V in which the two elements are added separately, one can see clearly that the addition of the two elements together increases the number of magnetite grains, whereas dendritic morphology becomes less pronounced.

IV. PARTITION OF THE TRANSITION ELEMENTS BETWEEN MAGNETITE AND SILICATE GLASS

Fig. 1 shows the results of EPMA analysis of Cr and Cu in magnetite and silicate glass when both are added separately. The numbers in the parenthesis, (I) and (II), indicate the starting composition I and II, respectively. Fig. 1 clearly demonstrates that Cr is characteristically concentrated in magnetite and the content increases with increasing the amount of Cr added. When more than 7.0 wt.% Cr is added to the starting composition, an anomaly appears, i.e. two different kind of magnetites, larger grains and very small grains, are found. The latter very minute magnetite grains (less than about 1.0 μm) containing a very small amount of Cr, in contrast to much higher concentration of Cr in the former larger chromian magnetite. Although some uncertainties still remain due to poor precision of the analytical data for smaller grains, the existence of this differentiation is undeniable. Cr content in the coexisting silicate glass, on the other hand, is very small (less than 0.5 wt.%) and the value remains almost constant with increasing the amount of Cr added. That is, K_{eff} $(=C_{magnetite}/C_{glass})$ is in the range of 50~80 for larger chromian magnetite and 6~9 for smaller grains. In both cases, K_{eff} is larger than unity. K_{eff} for Ti and Cu when they are added independently are 0.3~0.5 for Ti and 0.7~0.6 for Cu, respectively.

As compared to Cr, Cu concentrates more in the glass than in magnetite. The maxi-

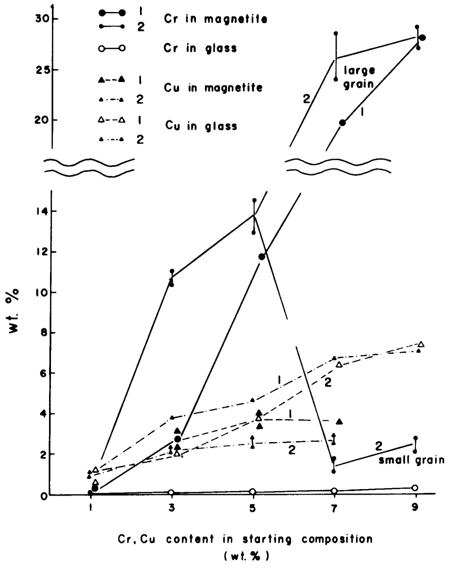

Fig. 1. Partition of Cr and Cu between magnetite and silicate glass. The two elements were added separately. Numbers in the figure (1 and 2) represent the composition I and II, respectively.

mum Cu concentration in magnetite is about 3 wt.%, which is obtained by the addition of 5.0 wt.% Cu. Further addition of Cu simply leads to the increase of Cu concentration in the glass, which becomes reddish-brown in color. K_{eff} for Cu is always smaller than unity.

When Cu and Cr are added together, Cr concentrates more remarkably in magnetite (Fig. 2), and Cu concentrates more in the glass than in the case that respective elements are added independently. Addition of Ti and Cu together causes high concentrations of the both elements in the glass (Fig. 3). Both elements have characteristic tendency to promote the development of dendritic or skeletal morphology.

Fig. 4 shows the partition of the three elements, Ti, Cr and Cu when they are added in

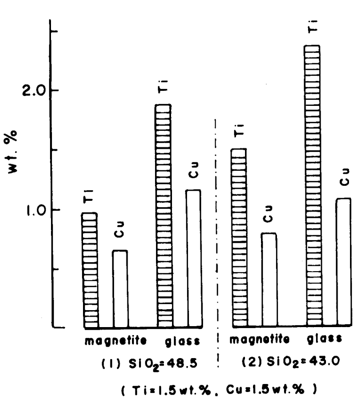

Fig. 2. Partition of Cr and Cu between magnetite and silicate glass. The two elements were added together.

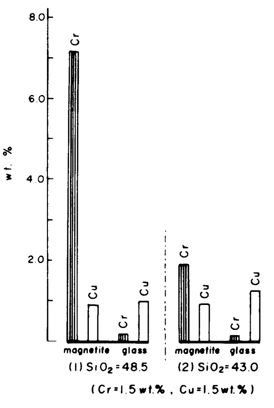

Fig. 3. Partition of Ti and Cu between magnetite and silicate glass.

combination. It is seen that Cr characteristically concentrates in magnetite, whereas Ti and Cu concentrate more in the glass.

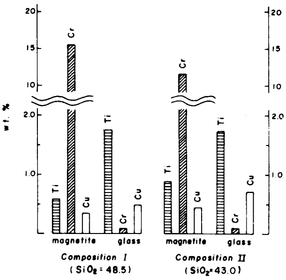

FIG. 4. Partition of Ti, Cr and Cu between magnetite and silicate glass. 1.0 wt. % of each element was added altogether.

V. DISCUSSION

The following relations are noted in the present study.

1) Ti and Cu promote the development of dendritic and/or skeletal morphology of magnetite.
2) Cr has a definite effect to decrease grain size, and increase the number of crystals.
3) Cr has $K_{eff}>1$ and definitely concentrates in magnetite.
4) Ti and Cu have $K_{eff}<1$, and concentrate more in the silicate glass.

Namely, transition elements with $K_{eff}>1$ (Cr) have an effect to promote nucleation, whereas those with $K_{eff}<1$ (Ti and Cu) to pronounce dendritic morphology. In addition to these, it should be mentioned that Ti and Cu have stronger effect upon the development of dendritic morphology to the composition I with higher viscosity than to the composition II with lower viscosity (cf. SHAW, 1972).

The elements with $K_{eff}>1$ have stronger affinity to magnetite structure than those with $K_{eff}<1$. Thus, they have tendencies to act as inhibitors (heterogeneous nucleation site) to form embryos of magnetite structure in the melt. This leads to increase the nucleation rate, and results in larger numbers and smaller grains of magnetite. On the other hand, transition elements with $K_{eff}<1$, i.e. Ti and Cu, will not play a role of inhibitors for the formation of magnetite embryos, but will be accumulated more at the interface between silicate melt and magnetite crystal as growth of magnetite proceeds. Due to constitutional supercooling, this accumulation will lead to a morphological instability of the interface, which will result in the development of dendrite. According to SUNAGAWA (1977, 1981a and b) and SUNAGAWA and BENNEMA (1981), σ^* and σ^{**} vary between the neighbouring branches. This is well demonstrated in the present experiments. As are seen in Figs. 1–A and B and Figs. 2–A and B in Plate V, the distance between the neighbouring branches becomes more and more close with increasing Ti and/or Cu content. The average distance of the neighbouring branches of dendritic magnetite produced by 1.0 wt.% Ti is about 1.5 μm. However, with increasing Ti content (3.0 wt.%), the neighbouring branches become closer drastically resulting almost saw-tooth morphology. In addtion, skeletal habit of coexisting plagioclase becomes more conspicuous with increasing Ti content (Fig. 1–B in Plate V).

According to SUNAGAWA (1977, 1981 a and b) and SUNAGAWA and BENNEMA (1981), σ^* and σ^{**} vary depending on (1) the phases from which crystals grow, (2) materials, (3) the ratio incorporation and diffusion rate k/D, and also α-factors which determine the interface roughness. In the present experiments, it has been demonstrated that skeletal and dendritic morphologies of magnetite, which are rarely encountered in natural igneous rocks, can be easily formed when transition elements, like Ti and Cu, with $K_{eff}<1$ are added. The addition of such elements probably modifies the interface roughness drastically through the accumulation process, and diminishes the values of σ^* and σ^{**} as compared to the values of the systems without these elements. Viscosity also has an effect to modify these values.

VI. CONCLUSION

Magnetite crystals with dendritic and skeletal morphologies are easily produced by the addition of transition elements with $K_{eff}<1$, Ti and Cu, to two silicate melts of basaltic compositions. The addition of the elements with $K_{eff}>1$, Cr, promotes the nucleation rate and diminishes the grain size. The effects of co-operation of these elements are also investigated. The effect of Cr can be accounted for as due to the formation of embryos, which act as heterogeneous nucleation sites. The effect of Ti and Cu to promote the development of dendritic morphology is explained as due to the concentration of these elements in the melt phase adjacent to the solid-liquid interface, which result in roughening of the interface, and the resultant decrease of σ^* and σ^{**} values (SUNAGAWA, 1977, 1981, 1982), as well as morphological instability. It is also observed that this effect is dependent upon the viscosity of the system.

The present result should be compared with the morphology of magnetite which crystallizes in the system without transition elements, i.e. impurities, which is now in progress.

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EXPLANATION OF PLATE V

FIG. 1. Dendritic and skeletal habit of magnetite produced by the addition of titanium (composition I).

A: Dendritic magnetite associating with plagioclase. Ti 1.0 wt. % added.
B: Dendritic magnetite associating with plagioclase. Ti 3.0 wt. % added.
C: Dendritic magnetite associating with pseudobrookite. Ti 5.0 wt. % added.
A, B and C are taken under the transparent light only.

FIG. 2. Effects of copper addition on the morphology of magnetite.

A: Dendritic magnetite coexisting with skeletal plagioclase. Cu 1.0 wt. %, composition I.
B: Ditto. Cu 3.0 wt. %, composition I.
C: Ditto. Cu 5.0 wt. %, composition I.
A and B are taken under both transparent and reflection light. C is taken under only transparent light.

EXPLANATION OF PLATE VI

FIG. 3. Effects of copper addition on the morphology of magnetite.

A: Skeletal magnetite coexisting with silicate glass. Cu 1.0 wt. %, composition II.
B: Ditto. Cu 3.0 wt. %, composition II.
A and B are taken under both transparent and reflection light.

FIG. 4. Minute crystals of magnetite formed by the addition of chromium to the composition II.

A: Cr 1.0 wt. %.
B: Cr 3.0 wt. %.
Both are taken under both transparent and reflection light.

EXPLANATION OF PLATE VII

FIG. 5. Morphological variation of magnetite appeared by the addition of transition elements in combination.

A: Composition II with Cr and Cu (1.5 wt. % each)
B: Composition I with Ti and Cr (1.5 wt. % each).
C: Composition II with Ti, Cr and Cu (1.0 wt. % each).
D: Composition II with Ti and Cu (1.5 wt. % each).
E: Ditto.
F: Composition I with Ti and Cu (1.5 wt. % each).

EXPLANATION OF PLATE V

FIG. 1. Dendritic and skeletal habit of magnetite produced by the addition of titanium (composition I).

A: Dendritic magnetite associating with plagioclase. Ti 1.0 wt. % added.
B: Dendritic magnetite associating with plagioclase. Ti 3.0 wt. % added.
C: Dendritic magnetite associating with pseudobrookite. Ti 5.0 wt. % added.
A, B and C are taken under the transparent light only.

FIG. 2. Effects of copper addition on the morphology of magnetite.

A: Dendritic magnetite coexisting with skeletal plagioclase. Cu 1.0 wt. %, composition I.
B: Ditto. Cu 3.0 wt. %, composition I.
C: Ditto. Cu 5.0 wt. %, composition I.
A and B are taken under both transparent and reflection light. C is taken under only transparent light.

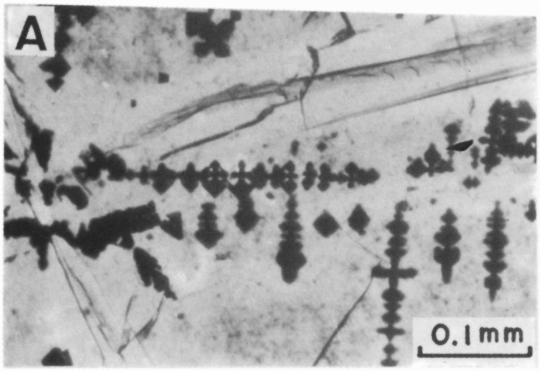

FIG. 1–A.

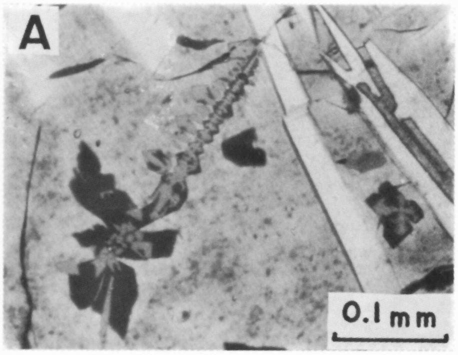

FIG. 2–A.

FIG. 1–B.

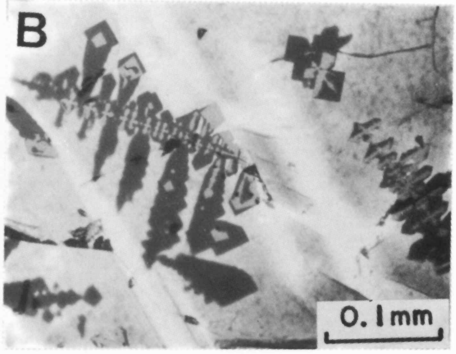

FIG. 2–B.

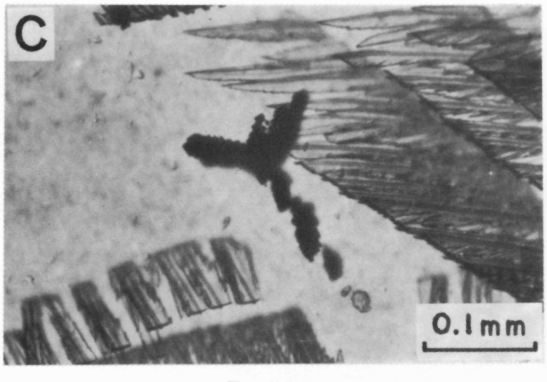

FIG. 1–C.

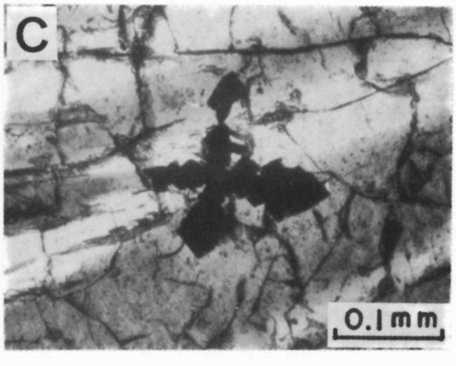

FIG. 2–C.

EXPLANATION OF PLATE VI

FIG. 3. Effects of copper addition on the morphology of magnetite.

A: Skeletal magnetite coexisting with silicate glass. Cu 1.0 wt. %, composition II.
B: Ditto. Cu 3.0 wt. %, composition II.
A and B are taken under both transparent and reflection light.

FIG. 4. Minute crystals of magnetite formed by the addition of chromium to the composition II.

A: Cr 1.0 wt. %.
B: Cr 3.0 wt. %.
Both are taken under both transparent and reflection light.

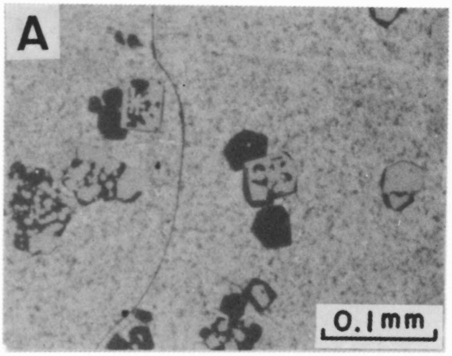

FIG. 3–A.

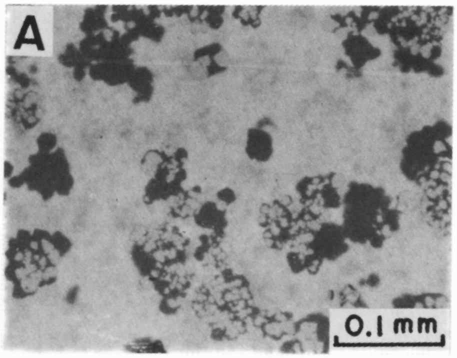

FIG. 4–A.

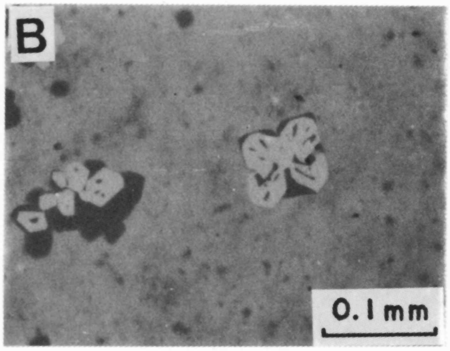

FIG. 3–B.

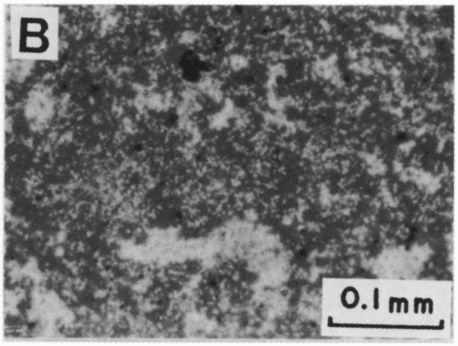

FIG. 4–B.

EXPLANATION OF PLATE VII

FIG. 5. Morphological variation of magnetite appeared by the addition of transition elements in combination.

A: Composition II with Cr and Cu (1.5 wt. % each)
B: Composition I with Ti and Cr (1.5 wt. % each).
C: Composition II with Ti, Cr and Cu (1.0 wt. % each).
D: Composition II with Ti and Cu (1.5 wt. % each).
E: Ditto.
F: Composition I with Ti and Cu (1.5 wt. % each).

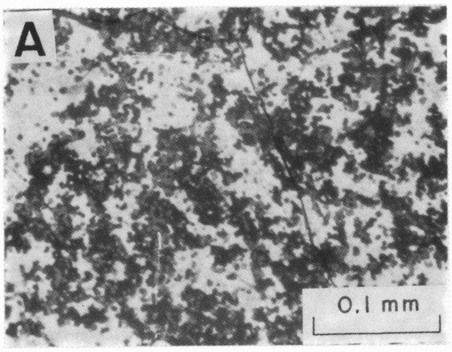

FIG. 5–A.

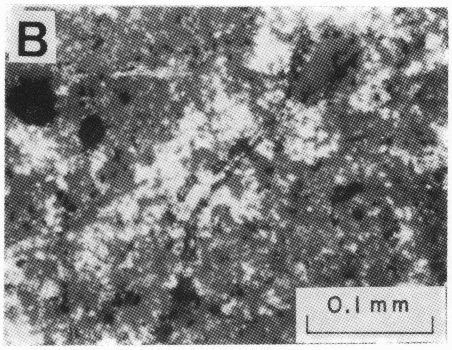

FIG. 5–B.

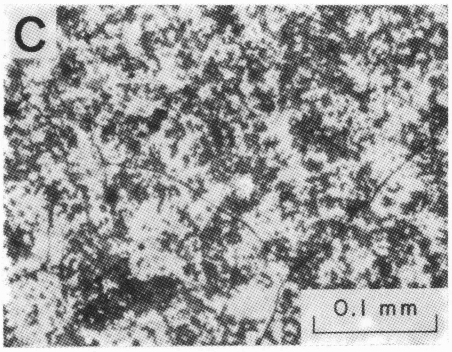

FIG. 5–C.

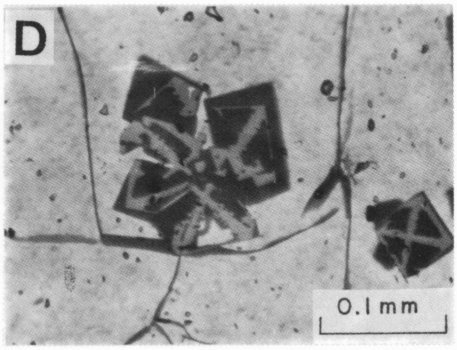

FIG. 5–D.

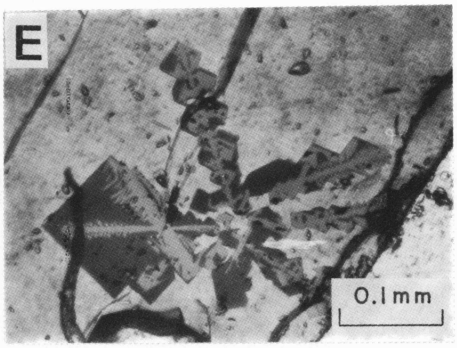

FIG. 5–E.

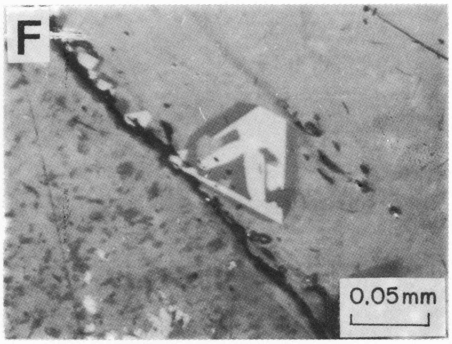

FIG. 5–F.